Removal of Toxic Elements and Microbial Contaminants from Groundwater Using Low-Cost Treatment Options

Dana A. Da'ana[1] · Nabil Zouari[1] · Mohammad Y. Ashfaq[1] · Mohammed Abu-Dieyeh[1] · Majeda Khraisheh[2] · Yousef M. Hijji[3] · Mohammad A. Al-Ghouti[1]

Abstract

Purpose of Review This paper reviews various low-cost treatment techniques such as adsorption, permeable reactive barrier, and biological techniques for the simultaneous removal of chemical and microbial contaminants from groundwater and discusses treatment mechanisms of different treatment techniques. This paper also discusses the challenges of groundwater treatment, how to choose the appropriate treatment technique, and cost analysis of groundwater treatment.

Recent Findings Various treatment technologies have been used for the treatment of groundwater: physical, chemical, and biological technologies with different success rates. In the literature, various adsorbents have been successfully synthesized from low-cost and environmentally friendly materials. Adsorption is considered an efficient treatment technique for the removal of both toxic elements and pathogens by utilizing different adsorbents. For example, the nanostructures of MgO with a BET surface area of up to 171 m^2/g obtained a very high adsorption capacity of 29,131 mg/g for fluoride ions in water, while the incorporation of iron in activated carbon has improved its adsorption capacity to 51.3 mg/g for arsenic. Moreover, certain adsorbents have shown the capability to remove 99% of the rotavirus and adenovirus from groundwater.

Summary Groundwater resources are contaminated with toxic metals and pathogens. Therefore, water treatment technologies should be evaluated for their efficiency to remove such contaminants. Determination of the most cost-effective and efficient treatment technique is not an easy task and requires the understanding of various aspects such as the contaminants present in water, the reuse options considered, and cost analysis of the treatment technique.

Keywords Groundwater · Toxic elements · Pathogens · Metals · Low-cost treatment techniques

Introduction

Throughout humankind's history, groundwater has been a highly crucial natural resource of fresh water, making 30% of global freshwater [1]. A significant freshwater percentage is supplied by groundwater to around 2 billion people, making around 40% of the irrigation water worldwide, as well as making about 50% of the world's municipal water [2]. Consequently, groundwater is currently under threat. Natural elements are present at higher levels in groundwater than in surface water due to the movement of groundwater throughout soil formations and rocks, dissolving various minerals and compounds [3•]. Overexploitation and unsustainable use of water especially in the Middle East and North Africa regions have caused groundwater depletion in the region (Table 1) [4], and what is left and available is contaminated which could be unsafe for human consumption or unfit for other purposes. Although utilization and degradation of groundwater quality have had significant attention around the world, a dramatic panorama has been generated from the poor management of water resources. By 2025, two-thirds of the population worldwide may live in water shortages [5•, 6]. The contaminations from both natural and anthropogenic sources further threaten their availability [7].

✉ Mohammad A. Al-Ghouti
mohammad.alghouti@qu.edu.qa

1 Department of Biological and Environmental Sciences, College of Arts and Sciences, Qatar University, P.O. Box 2713, Doha, Qatar

2 Department of Chemical Engineering, College of Engineering, Qatar University, P.O. Box 2713, Doha, Qatar

3 Department of Chemistry and Earth Sciences, College of Arts and Sciences, Qatar University, P.O. Box 2713, Doha, Qatar

Table 1 Total groundwater resources and its withdrawal rates in 2017 [4]

	North Africa	Sub-Saharan Africa	Central America	North America	South America	Asia	Middle East (Arabian Peninsula)	Eastern Europe	West and East Europe	Oceania
Total groundwater (10^9 m^3/year)	15	1404	222	1903	2475	3202	5	837	513	93
Groundwater withdrawal (10^9 m^3/year)	25	6.5	4.5	147	24	594	28	13	42	7.5

The types of natural contaminants and their concentrations depend on the geological nature of the materials, through which the groundwater flows, as well as the recharge water quality. The movement of groundwater through soils and sedimentary rocks can result in the release of a wide variety of contaminants, which affect the quality of water [8]. Since groundwater is a highly complex system with the interference of various variables and processes, understanding the relationships between groundwater, land-use, and contamination needs an advanced assessment tool. According to Verma et al. [9], the quality of groundwater depends on several different essential features, for example, natural or geo-genic factors such as native geomorphology and type of the sediment and minerals as well as the anthropogenic conditions including patterns of land-use. Microbial contaminants from animal and human waste could be another contamination source that can spread bacteria and parasites like microscopic worms and protozoa, as well as viruses [8]. Because of the complicated systems of groundwater and the change in its quality, a worldwide concern about groundwater quality is growing due to the importance of water in life. Thus, treatment of groundwater is highly significant, as, to sustain the social and economic development, water resources with high quality are considered very crucial factors [10].

Table 2 summarizes the presence of toxic metals and other elements in groundwater in different regions of the world. It is clear from Table 2 that the presence of these metals and chemical contaminants is a serious threat to the global groundwater resources. In comparison to the WHO (2017) [11] and USEPA (2018) [12] standards, several countries have reported higher concentrations of metals than the permissible limits. For example, the maximum concentration of boron was found to be 49.3 mg/L (mean value: 2.434 mg/L) in Saudi Arabia [13•] and 3.819 mg/L (mean: 1.885 mg/L) in Qatar [14••], much higher than the permissible limit of 2.4 mg/L (Table 2). Similarly, the concentration of lead in groundwater of Bangladesh [15••], China [16], Nigeria [17], and Pakistan [18•] is several orders of magnitude higher than the permissible limits (Table 2). This shows that the contamination of groundwater with these metals requires global attention.

Many researchers have also shown the contamination of groundwater with pathogenic microorganisms (bacteria, viruses, and protozoa) (Table 3). The presence of these bacteria such as V. cholera and Salmonella and viruses like hepatitis A virus, rotavirus, and adenovirus in water shows the potential of groundwater to cause various disease outbreaks in the exposed population.

Various treatment technologies have been used for the treatment of groundwater comprising physical, chemical, and biological technologies with different success rates. Physical treatments of groundwater include volatilization, ultrafiltration or filtration, incineration, and adsorption. Chemical techniques include precipitation, redox reactions,

Table 2 Concentration of heavy metals and other elements in groundwater reported worldwide in comparison with the WHO and USEPA standards

Elements (μg/L)	Bangladesh (Dhaka) [15]	China (Dongting Lake plain) [16]	China (Guanzhong Plain) [19]	India (Tamil Nadu) [20]	Iran (Southeastern) [21]	Nigeria (Ogun) [17]	Pakistan (Northern) [18]	Qatar [14••]	Saudi (Red Sea coast) [13•]	WHO 2017 [11]	USEPA 2018 [12]
Arsenic	2	7.4	1.095	-	15.5	-	-	2	4	10	10
Aluminum	-	540.25	1.625	-	-	-	-	1.5	-	200	200
Boron	-	-	-	-	-	-	-	1885	2434	2400	6000
Copper	9.6	1.7	1.88	40	0.65	36	-	1.37	7.69	2000	1300
Cobalt	-	0.03	0.165	-	-	-	171	-	-	-	-
Chromium	1.5	21	21.535	30	8.75	16	89	3.912	1.27	50	100
Cadmium	-	0.3	0.03	-	-	10	59	-	0.16	3	5
Fluoride	-	-	-	-	-	-	-	3.81	-	1500	4000
Iron	89.6	1076.5	28.005	260	8	708.5	1468	4.72	-	-	300
Lithium	-	-	-	-	-	-	-	0.1206	-	-	-
Manganese	58.8	434.5	10.32	-	1.32	156	627	1.009	-	400	30
Molybdenum	-	0.4	6.28	-	-	-	-	53.88	-	70	40
Nickel	-	0.32	0.945	-	7.23	82	92	1.94	25.62	20	100
Selenium	-	-	-	-	4.3	-	-	8.882	86.58	40	50
Lead	49.6	9.1	0.195	-	-	449.5	55	-	7.11	10	1.5
Vanadium	-	-	4.07	-	-	-	-	14.36	-	-	-
Zinc	5.3	1025.5	213.91	30	1.83	137.5	3738	5.88	57.9	3000	5000
Phosphates	60	-	-	-	-	-	-	-	0.01	-	-
Sulfates	11230	-	-	-	487	-	-	4977.2	1138.24	250000	250000
Nitrates	-	-	-	-	13.7	-	-	36.32	22.64	50000	10000

or ion exchange, while biological treatment can be carried out by using bioreactors or in slurry phase systems [29]. The technologies that are commonly used in the treatment of groundwater either have high treatment costs, produce harmful by-products, or energy-intensive [30, 31]. For instance, the ion exchange technique is a promising technique for the treatment of water with no generation of sludge, but this process is limited to specific pollutants as well as requires high cost for the replacement of the resin over time. Although the membrane filtration process is efficient in water treatment and can have high removal capacities without the generation of secondary pollution, its high manufacturing costs, severe fouling, and high-energy consumption are major drawbacks that limit its application. Therefore, much research is focusing on the use of more economic and environmentally friendly sustainable treatment techniques [32].

Based on our knowledge, there is no review paper that discusses the low-cost treatment techniques used for the simultaneous removal of chemical and microbial contaminants from groundwater. Therefore, this paper reviews the cost-efficient treatment techniques and the removal mechanisms of certain contaminants by the techniques, as well as the challenges and cost analysis of groundwater treatment.

Simultaneous Removal of Toxic Elements from Groundwater Using Low-Cost Treatment Techniques

The presence of certain elements such as fluoride, and heavy metals like arsenic, boron, and lead in groundwater is a major concern for environmental and public health. The groundwater contaminated from such elements, when used for irrigation and drinking purposes, may lead to toxic impacts on plants, animals, and humans. Therefore, the removal of such elements from groundwater should be considered before its application. There are various chemical, physical, and biological techniques that have been proved to be cost-effective and highly efficient in the treatment and simultaneous removal of multi-elements and microorganisms from groundwater. Among these techniques, adsorption, permeable reactive barrier, membrane distillation, electrocoagulation, and biological remediation will be discussed in detail.

Treatment of Groundwater by Adsorption

Adsorption is considered the best treatment technique for the removal of contaminants from water due to its higher removal

Table 3 Detection of pathogens in groundwater

No.	Study area	Pathogens detected	
1	Africa (sub-Sahara) [22]	Bacteria	*A. muciniphila, A. butzleri, Enterococcus faecium, Bifidobacterium longum, C. freundii, Desulfovibrio desulfuricans, Enterococcus gallinarum/casseliflavus, Vibrio cholerae, Salmonella enterica*
2	Italy (Campania) [23••]	Virus	Hepatitis A virus, human adenovirus, astrovirus, norovirus GI, GII, Aichivirus, rotavirus, sapovirus
3	Canada (Ontario) [24]	Bacteria	*Proteobacteria, Omnitrophia, Patescibacteria, Rokubacteria, Nitrospirae, Cyanobacteria*
4	China (Jianghan Plain) [25]	Bacteria	*Campylobacter* sp., *E. coli, L. pneumophila, L. rubrilucens, L. feeleii, L. anisa, V. cholera*
5	Southwest Nigeria [26]	Bacteria	Fecal coliform, *E. coli*, Fecal Streptococci
6	Sri Lanka (Anuradhapura, Monaragala, Kandy) [27]	Bacteria	*Proteobacteria, Bacteroidetes, Actinobacteria, Firmicutes, Cyanobacteria*
7	USA (Minnesota) [28••]	Bacteria	Bacteroidales, *Campylobacter jejuni*, Shiga toxin 2-producing bacteria, *Salmonella*
		Virus	Adenovirus, human enterovirus, human polyomavirus, norovirus, bovine polyomavirus, pepper mild mottle virus, rotavirus group A
		Protozoa	*Cryptosporidium* spp., *Giardia duodenalis* assemblage

efficiency, cost-effectiveness, lesser energy consumption, and low waste generation. Due to the possibility to produce adsorbents from renewable resources, ease in operation of the adsorption process, and low toxicity, the adsorption technique possesses a broader prospect for application in the removal of metals from water [33]. In the literature, the adsorption behaviors of soluble heavy metals and elements such as arsenic, boron, chromium, cadmium, lead, zinc, and fluoride are widely studied [34••].
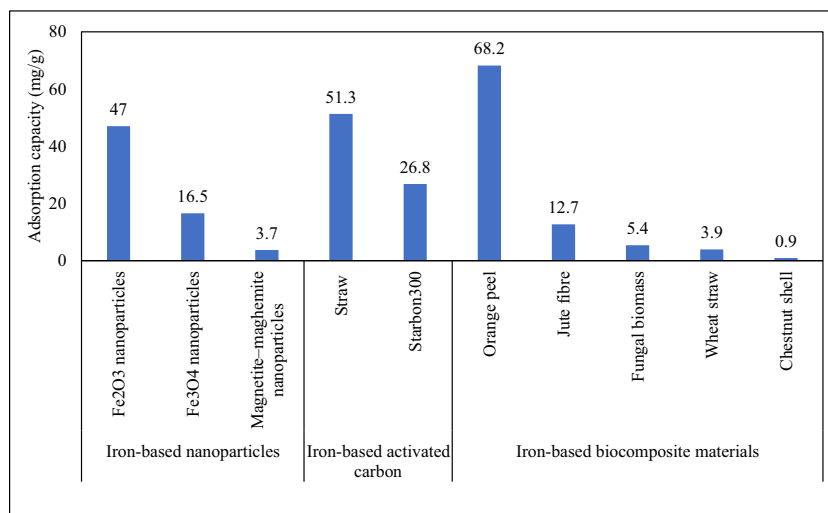
Removal of Arsenic

The presence of arsenic in groundwater is of great concern as it can cause toxicity even at a very low concentration of < 100 μg/L. Moreover, the removal of arsenic is a must if the concentration is higher than 10 μg/L in water intended for drinking purposes [35]. Arsenic contamination in groundwater can occur from both natural and anthropogenic sources. The natural sources may include ferrous rocks, iron-pyrites, and resulting sediments. The most commonly found arsenic-containing mineral is arsenopyrite, desorption of which releases arsenic into the groundwater. On the other hand, the anthropogenic sources include industrial and domestic waste, agricultural and mining activities, leachates from landfills, and burning of coal [36]. Arsenic commonly exists in two forms, i.e., arsenite (As(III)) and arsenate (As(V)). Arsenite is considered more toxic due to its water solubility than the organic/inorganic form of arsenate [35].

The adsorbents derived from natural sources such as eggshell, tea waste, and pomegranate peels among others have been successfully utilized for the removal of arsenic from water. Maity et al. [37] demonstrated a comparative assessment on the removal of arsenic from groundwater by natural magnetic material (NMM) (rock) and synthesized magnetic material (SMM) by humic acid and *Bacillus pasteurii*. Results showed that, within 120 min, both NMM and SMM were able to achieve arsenic removal efficiency in the range of 90 to 100%, but it was observed that NMM exhibited very fast arsenic removal, as it was capable to remove up to 87% within 30 s. Therefore, easy removal of arsenic can be achieved by utilizing NMM and because of the particle's magnetic properties; the adsorbent can be separated from arsenic-free water after the arsenic removal. The obtained results indicated the applicability of the eco-friendly and cost-effective NMM green material for the treatment of arsenic-contaminated groundwater.

In the literature, various adsorbents (iron-containing compounds, activated carbon, and fly ash) have been reported to achieve a high adsorption capacity of 150 mg/g [35]. The loading of iron into the adsorbents has helped to improve the adsorption capacity for arsenic as a result of co-precipitation mechanisms. Figure 1 shows various iron-based adsorbents

Fig. 1 Adsorption capacity of iron-based adsorbents tested for the removal of arsenic from water [40–49]

(activated carbon, biocomposites, and nanoparticles) that have shown to have an affinity towards adsorption of arsenic, As(III). Similar results have also been reported for As(V). For example, the use of activated carbon achieved 55% removal of As(V), while, the loading of iron onto the activated carbon improved the % removal up to 97% [38]. Callegari et al. [39] investigated the simultaneous removal of both As(V) and As(III) from groundwater. In this study, an iron oxide–coated sand column filter was utilized for the removal process where the experimental tests gave satisfactory results with removal rates that reached 99%.

Removal of Boron

Boron is a commonly found contaminant in both seawater and groundwater, where its concentration varies from 0.3 to 100 mg/L in groundwater. Boron exists as part of compounds since elemental boron has not been found yet. It is commonly used in many industries such as the glass industry, pharmaceutical industry, and cosmetics industry. According to the WHO, the concentration limit for boron is 2.4 mg/L [50••].

Various types of adsorbents (activated carbon, chelating resins, fly ash, and those derived from natural sources) can be used to separate boron from water even at very low concentrations. Table 4 provides a summary of adsorption capabilities, experimental conditions, and isotherm models for some selected adsorbents. Chen et al. [51] used magnetic magnetite nanoparticles (MMN) as an adsorbent to remove boron. The MM nanoparticles were synthesized by facile co-precipitated method with super magnetism and high specific surface area. It was found that the adsorption was endothermic, spontaneous chemisorption process, which was dominated by the external film diffusion and entropy change instead of the enthalpy change. Furthermore, adsorption equilibrium was rapid as it was achieved within 1.5 h with approximately 50

mg/g equilibrium capacity at pH 7 and 45 °C. The MNN is found to be a promising agent for the removal of boron as it has low cost and easy regeneration and can be separated by an external magnetic field, as well as having satisfactory mechanical strength.

Removal of Fluoride

The contamination of fluoride in groundwater is considered one of the most significant problems in the world. Fluoride exists in a variety of forms which include fluorite (CaF_2), cryolite (Na_3AlF_6), and fluorapatite ($Ca_5(PO_4)_3F$), and release of fluoride occurs as a result of its dissolution in groundwater under variable chemical conditions. The concentration of fluoride exceeding 1.5 mg/L can be harmful to humans, as per the WHO recommendation [60].

Adsorption techniques using a variety of adsorbents including nanomaterials, metal composites, and adsorbents derived from organic sources have been used for the defluoridation of water (Table 5). For example, the pristine and magnetic biochar by peanut hull and bovine bone was synthesized for the adsorption of fluoride from groundwater [61]. The results showed that higher adsorption capacity was achieved when preparing magnetic biochar by soaking in $FeCl_3$ solution and then pyrolyzing compared to when mixing pristine biochar with a Fe^{2+}/Fe^{3+} solution and then treating with NaOH. The high adsorption capacity of fluoride by both bone-derived biochar and magnetic biochar can be attributed to the presence of γ-Fe_2O_3 and hydroxyapatite (HAP) that formed during the charring bones. Similarly, Pigatto et al. [62] also developed an environmentally friendly and cost-efficient technique for the removal of fluoride from groundwater, namely adsorption onto calcined sludge. The results showed that, under the optimum experimental conditions of 5 g/L as adsorbent dosage and a pH of 5.5, the maximum adsorption capacity was more

Table 4 Adsorption capabilities, experimental conditions, and isotherm models for some selected adsorbents for removal of boron from water

No.	Adsorbent		Adsorption capacity (mg/g) or % removal efficiency	Isotherm model and adsorption kinetics	Remarks	Ref.
1	Resins	Polyvinyl alcohol (PVA)	26.7 (mg/g)	Freundlich	Glucose as functional group	[52]
		Polyallylamine (PAA)	32.9 (mg/g)	Freundlich	Glucose as functional group	[53]
		Glycidyl methacrylate-dehydrochlorinated polyvinyl (GMA-DHPVC)	27 (mg/g)	Pseudo-second order	Iminodipropylene glycol as functional group	[54]
2	Natural adsorbents	$FeCl_3$-modified waste calcite	1.6 (mg/g)	Langmuir and Freundlich	pH: 9, adsorption time: 1440 min	[55]
		Rice residues	9.26 (mg/g)	Langmuir and Freundlich	pH: 8, adsorption time: 2880 min	[55]
		HCl-modified sepiolite	178.57 (mg/g)	Langmuir, Thomas model and Yoon and Nelson model	pH: 10, temperature: 20 °C	[56]
		Calcium alginate gel	94 (mg/g)	Langmuir, Pseudo-second order	pH: 9–10, dosage: 0.2 g/100 mL	[57]
3	Fly ash	Fly ash	94 (%)	Langmuir and Freundlich and Pseudo-second order	pH: 10–11, dosage: 100 g/L, adsorption time: 1500 min	[58]
		Concrete particles	99.8 (%)	-	Temperature: 175 °C, adsorption time: 1440 min, initial concentration: 10 mg/L	[59]

than 70%, which was enough to attain the WHO limits of 1.5 mg/L. The WHO limit was achieved within 60 min. Thus, these results indicated the ability to use calcinated sludge as an environmentally friendly and low-cost adsorbent for the treatment of groundwater.

In addition, Ayinde et al. [63••] synthesized a multi-functional 3-layered Ag-MgO/nanohydroxyapatite (Ag-MgOnHaP) composite for the removal of fluoride and bacteria from groundwater. *Citrus paradisi* peel extract was used for the reduction of Ag and MgO ions and impregnation of Ag-MgO nanoparticles on the surface of the adsorbent. Results showed that 90% fluoride removal was achieved by using the synthesized adsorbent. The best-fit isotherm model for the experimental adsorption data was the Freundlich isotherm model indicating that adsorption happened on a multi-layered heterogeneous surface. Table 5 summarizes the highest adsorption capacities (mg/g) obtained for fluoride and reported in the literature at variable concentrations, contact time, and pH.

Removal of Multiple Toxic Elements from Groundwater

Besides arsenic, boron, and fluoride, there are many other elements and toxic metals that have been reported in the literature (Table 2). Some researchers have also attempted to develop novel low-cost adsorbents for the simultaneous removal of these elements from groundwater. For example, Arancibia-Miranda et al. [92••] investigated the synthesis of iron oxide–functionalized magnetic imogolite nanocomposite for the simultaneous removal of copper, cadmium, and arsenic from groundwater. The physicochemical properties for the prepared nanocomposite showed that the size and distribution of the magnetite nanoparticles were mainly dependent on the concentration of Fe^{3+} rather than the presence of aluminosilicate in which a higher concentration of Fe^{3+} favored the 3-dimensional growth of Fe-oxides with multilayer formation. The isotherm studies showed that there were at least 4 kinds of adsorption sites that held variable metal selectivity, namely preferential copper sites, preferential cadmium sites, arsenate preferential sites, and non-preferential sites for copper, cadmium, or arsenate. Moreover, this study compared the use of adsorbent in multi-component systems and a single-component system and found that a 12% decrease in adsorption of copper by imogolite resulted in a multi-component system as compared to the single-component system, while cadmium exceeded 41% in the same case. This could be attributed to the chemical characteristics of the adsorbate in the affinity of these metal ions towards ≡ Al – OH and ≡ Si-OH groups conditioned by their ionic radius, polarizability, and electronegativity. Similar behavior was observed when the synthesized nanocomposite was used, but a slight decrease

Table 5 Adsorbents with the highest adsorption capacities for fluoride in water

No.	Adsorbent	Adsorption capacity (mg/g)	Concentration (mg/L)	Contact time (min)	pH	Reference
1	Porous MgO nanostructures	29,131	10	5	7	[64]
2	Aluminum fumarate MOFs	600	1–100	1440	2–7	[65]
3	Hydroxyl aluminum oxalate (HAO)	400	20	239	6.5	[66]
4	TiO_2/graphene	342	10–150	60	6	[67]
5	Fe-La-Ce trimetallic composite	303.03	10–100	120	4	[68]
6	ZrO_2 mesoporous fibers	297.7	5–300	150	3	[69]
7	Integrated UiO-66/CF hybrid	295	5–200	240	7	[70]
8	Hierarchically meso-/macroporous MgO	290.67		30	2–10	[71]
9	La/Mg/Si-loaded palm shell-based activated carbon (LMSAC)	285.7	100	120	7	[72]
10	Pectin based Fe-Al-Ni trimetallic oxide	285	20–100	40	2–10	[73]
11	Ca-loaded hydrophilic hyper-cross-linked porous polymer networks (HHCP1)	267	50–2000	360	3–7	[74]
12	Ce-modified Luffa cylindrica (LC-Ce)	212	10–30	10–60	7	[75]
13	Phenolic-functionalized hollow sponge-like adsorbent (HSLW)	200.1	20	1080	5	[76]
14	Alginic-based Fe-Al-Ni trimetallic oxide	200	20–100	50	2–10	[73]
15	Boron-doped biochar/Al_2O_3	196.1	20	-	3–8	[77]
16	Ce (IV)–incorporated hydrous Fe (III) oxide modified graphene oxide (GO-CIHFO)	190.61	5–60	180	3 and 7	[78]
17	La-loaded chelating resin	187	1.5–50		4–5	[79]
18	Hierarchy flowerlike zeolite	161	1.05–51.7	30	2	[80]
19	Magnesium silicate ($MgSiO_3$) modified palm shell activated carbon powder (MPSAC)	150	5–125	120	5	[81]
20	Chemically treated carbonized bone meal	150	10	1440	6.1	[82]
21	Single-walled carbon nanotubes (SWCNTs)	50–150	100	45	6	[83]
22	Mg-Al-Ce triple-metal composites	124.89	50–120	180	3–10	[84]
23	Hydrous CeO_2-Fe_3O_4 decorated polyaniline fibers nanocomposite	117.64	5–100	40	3–10	[85]
24	Lanthanide-based MOFs	103.95	0–200	10	3–7	[86]
25	Zr-MOFs	102.4	1–200	20	7	[87]
26	Flue gas desulfurization gypsum	96.9	7.3–109	10	5–11	[88]
27	$Al(OH)_3$ nanoparticles modified hydroxyapatite (Al-HAP)	93.84	200	1440	7	[89]
28	3MgAlFe-cal phase	92.3	10–50	420	9.3–10.7	[90]
29	Magnetic core-shell Ce-Ti@Fe_3O_4	91.04	1–500	< 15	5–11	[91]

in cadmium adsorption difference between the single- and multi-component systems due to the electrostatic effects and changes in nanocomposite porosity, as well as the presence of $\equiv Fe - OH$ groups. Furthermore, arsenate presence in the system favored the divalent metal removal such as copper and cadmium in which its existence modified the selectivity and affinity of the original active sites of both the imogolite and the synthesized nanocomposite. This could lead to a reduction in the common sites' density of copper and cadmium. However, it generates specific sites for each metal affecting the adsorption macroscopic behavior.

Besides, Khalfa et al. [93] evaluated the efficiency of natural and activated clay for the simultaneous removal of lead, copper, zinc, and cadmium from groundwater. An affinity order of $Pd^{2+} > Cu^{2+} > Zn^{2+} > Cd^{2+}$ was obtained from the adsorption experiments results. The preferential lead removal over other metals could be due to the effect of metal physicochemical properties on the removal mechanism such as electronegativity, atomic radius, constant hydrolysis, and relative binding strength.

Bortone et al. [94] combined the use of advanced drainage systems with adsorption termed as in situ reactive drainage systems for groundwater treatment (In-DRAIN-TREAT). This process took into consideration the natural gradient of groundwater for the passive treatment process in which a drainage system was used for collecting the contaminated groundwater by means of horizontal drains that are located longitudinally to the flow direction, which in turn directs it to a waterproofed cell. This was directly treated into an active cell that is located downstream to avoid any external energy inputs. This study compared the use of this innovative treatment system with a permeable reactive barrier technology for the removal of hexavalent chromium. Their preliminary results showed that the use of treatment cells filled with activated carbon and with no energy consumption was applicable and efficient in the treatment process as it showed a 10% reduction in the remediation costs.

Abraham et al. [95] explored the removal of Fe(II) from groundwater by using ferric hydroxide [$Fe(OH)_3$] flocs as media for the adsorptive removal process. In this study, Fe(II) is directly adsorbed on $Fe(OH)_3$ precipitate, as it is converted to Fe(III) and subsequently the hydrolysis of $Fe(OH)_3$ causing the formation of a new surface for further adsorption. Therefore, the frequent replacement or maintaining of the media was not required as well as the un-needed backwashing process, which in turn makes this method more cost-effective. Results indicated that this method was significantly efficient in removing Fe(II) from groundwater. However, the presence of competitive ions such as Ca^{2+} and Mn^{2+} can reduce the adsorption efficiency while ions such as SO_4^{2-}, Cl^-, and F^- had no significant competitive effect on the adsorption process. Moreover, Elkady et al. [96] synthesized a magnetic hybrid adsorbent matrix for the simultaneous

adsorption of iron and manganese ions from groundwater. In this study, magnetic hydroxyapatite (HAP) nanocomposites were synthesized by co-precipitation and microwave method; two adsorbents were prepared, namely HAP and advanced magnetic hydroxyapatite (MHAP). The results indicated superior adsorption behavior of MHAP toward both iron and manganese ions with removal efficiencies of 98% and 95%, respectively, while HAP achieved 86% and 80% for the removal of both iron and manganese, respectively.

For the efficient removal of lead, cadmium, and zinc from groundwater, Holmes et al. [97] explored the incorporation of lime softening wastes as recycled drinking water treatment wastes (DWTW), and low-cost additive to replace the ordinary Portland cement (OPC) with cement-based filter media (CBFM). The results showed 100% removal of the three heavy metals from groundwater by the novel adsorbent at low concentrations of DWTW (0.01 mM); however, increasing the concentration of DWTW (1.00 mM) leads to a decrease in the removal efficiency. This could be attributed to either the saturation or the exhaustion removal mechanism. It is illustrated from the study that DWTW has the potential to be used as an enhancement for CBFM as this incorporation has a large sequestration capacity to lead, cadmium, and zinc through insoluble carbonate formation.

It is strongly indicated from the obtained results that the used adsorbents were successfully synthesized from low-cost and environmentally friendly materials. To conclude, adsorption is considered an efficient treatment technique for the removal of various contaminants from groundwater by utilizing different adsorbents. However, prior to the implementation of the adsorption process for the treatment of groundwater, the cost of adsorbent regeneration should be considered, as some regeneration processes are energy-intensive and costly. In such cases, other treatment options should be investigated such as biological treatment techniques. Although the applicability and efficiency of the adsorption technique on the treatment and removal of different contaminants from groundwater are proved, this technique is unable to continuously produce potable water with high quality because it is limited in the simultaneous removal of contaminants especially those present in saline groundwater. Hence, the application of membrane techniques as a post-treatment technique must be considered for such cases.

Treatment of Groundwater by Permeable Reactive Barrier

Permeable reactive barriers (PRBs) are widely implemented, cost-effective, and viable technology where contaminated groundwater flow is not restricted as it passes over the reactive fluid, i.e., barrier material, for the immobilization or passive contaminant degradation. A variety of materials can be used

as reactive materials for groundwater treatment such as zerovalent iron, limestone, microorganisms, straw, peat, and various other materials [98]. According to Zhang et al. [99], a PRB enables the contact of the contaminated groundwater with the adsorptive material, which is inserted underground in a natural aquifer in which the contaminants are removed by intercepting the pollution plume and without water pumping. Therefore, this valuable innovative technology is considered cost-effective, environmentally friendly, and more economical over the long term when compared with other techniques that require energy input continuously.

Falciglia et al. [100] investigated the potential use of a novel microwave-based regenerating permeable reactive barrier (MW-PRB) system for the removal of cesium (Cs) from groundwater with the use of activated carbon as an adsorbent in both batch experiments and column MW-regeneration experiments. The results showed that 80% removal of Cs was achieved with the column experiments when activated carbon was irradiated for 15 min. Moreover, it was revealed by the techno-economic analysis that this technique is feasible and advantageous compared to the conventional PRB system as the saved cost confirms the cost-effectiveness of the MW-PRB system encouraging the implementation of this technique.

Maamoun et al. [101] investigated the use of PRB for the removal of Cr(VI) from groundwater by using 4 reactive materials, namely nanoscale zerovalent iron (Fe°), bimetallic nanoscale zerovalent iron (Fe°/Cu), activated carbon, and sand/zeolite mixture. Results showed the superiority of Fe° over other reactive materials with a Cr(VI) removal efficiency of 89.7%. Meanwhile, Fe°/Cu, activated carbon, and the sand/zeolite mixture had a removal efficiency of 84.1%, 23.01%, and 14.0%, respectively. Faisal et al. [102] converted inert sand into a reactive material by coating the surface with humic acid nanoparticles that were extracted from sewage sludge. The coated sand-humic acid (CSHA) ability for the simultaneous removal of copper and cadmium from groundwater was investigated. Results showed that CSHA had a maximum adsorption capacity of 87.5 mg/g for copper and 18.9 mg/g of cadmium with removal efficiencies of more than 98%. Moreover, the results indicated that the predominant mechanism for the treatment process was the physisorption process.

Wen et al. [103] suggested the use of raw straw agricultural waste as a potential PRB carbon source because of its high content of elemental carbon. In this study, straw zerovalent iron and zerovalent iron-free sustainable-release carbon-compound material (ZVI-free SCCM) were used as field PRB fillers to determine their ability in reducing nitrogen transport from shallow groundwater to surface water. Results indicated the potential efficiency of the used filler to remove nitrogen as well as avoid the problem of secondary pollution, such as high ammonium nitrogen concentration in the treated groundwater. The results showed that more than 60% of nitrogen was removed from groundwater; therefore, straw waste can be a sustainable filler matrix alternative to the widely used wood chips in the PRB system.

The use of a granular mixture of ZVI and lapillus at different weight ratios (30:70 and 50:50) as a reactive media in PRB through column experiments was tested [104]. Higher iron content (50:50) of the ZVI/lapillus mixture had a higher reduction of the hydraulic conductivity over time but had higher removal rates. Results represented the efficiency of the two used reactive media in removing the studied pollutants according to the following sequence: Cu > Zn > Ni. This removal behavior could be attributed to the affinity of iron oxides and hydroxides towards the 3 contaminants. Different removal mechanisms were responsible for the removal process. The removal of copper from contaminated groundwater could be due to the cementation process that occurred at the surface of ZVI when iron (hydro)oxide was not covering it which in turn prevented the electron transfer. Moreover, quantitative removal of nickel, zinc, and copper could be due to the precipitation mechanisms as they can precipitate as hydroxides when the pH of the flowing water through ZVI increases, or by adsorption onto the surface of (hydro)oxide, or by the co-precipitation with iron hydroxides.

Permeable reactive barrier treatment techniques can treat groundwater in biological, physical, or chemical processes. This treatment technique is effective for contaminants that are not deeper than 20 m beneath the ground surface and it might require the replacement or removal of the reactive media during operation. Moreover, the effectiveness of this treatment technique depends on the pH range of the barrier chemical which should be selected based on the used sorbent and the metal removed. This could be a limiting factor when removing multiple contaminants at the same time. Furthermore, zerovalent iron is the most used reactive material; however, the production of this material is energy-intensive leading to an increase in the environmental effects of the permeable reactive barrier process. In addition, more research is recommended to be carried out on the effect of pH, temperature, and dissolved salts on the removal efficiency of this technique. Therefore, further research is required for the use of low-cost natural products as reactive materials for the simultaneous removal of multi-elements and microorganisms from groundwater by a permeable reactive barrier.

Treatment of Groundwater by Membrane Distillation

The membrane distillation (MD) process is thermally driven where water vapor molecules pass through a porous hydrophobic membrane. This process is enhanced by inducing the vapor pressure by the difference in temperature across the membrane,

which in turn reaches solution saturation without a significant decline in the flux [105]. Moreover, this technique utilizes low-grade energy for operation, which can be generated by waste-grade energy, solar energy, or geothermal energy. Thus, it is considered an efficient and cost-effective alternative treatment process when compared to other conventional membrane processes [106]. Synthesis of MD membranes occurs by using different methods such as phase inversion and electrospinning techniques by using hydrophobic polymers like polyvinylidene fluoride (PVDF), polypropylene (PP), polyethylene (PE), or polytetrafluoroethylene (PTFE). Modification with nanoscale materials such as silver, silica, and titania as well as graphene and carbon nanotubes (CNTs) significantly enhances the performance of the MD membranes and its hydrophobicity, prevents wetting and fouling, and improves the membrane mechanical strength. Various methodologies can be used for modifying the MD membranes, namely dip coating, graft polymerization, and interfacial polymerization [107].

Mishra et al. [108] synthesized and introduced ferrous sulfide (FeS) and carboxyl-functionalized ferroferric oxide (CFFO) nanoparticles into PVDF membrane through phase inversion technique and produced 3 membranes, namely FeS/PVDF, CFFO/PVDF, and FeS/CFFO/PVDF. In this study, the prepared membranes were examined for the simultaneous removal of lead, cadmium, and chromium from groundwater. Results showed that the synthesized membranes had enhanced porosity, good mechanical and thermal stability, high water flux, and high water uptake capacity, as well as high efficiency in the removal of the three tested pollutants. Furthermore, among the three prepared membranes, FeS/CFFO/PVDF membrane showed the highest efficiency for the simultaneous removal of lead, cadmium, and chromium from real groundwater with a removal percentage of 98.7%, 96.4%, and 95.4%, respectively. In addition, the developed membrane was able to remove total arsenic from the tested real groundwater with an excellent removal efficiency of 95.9%.

Moreover, low-cost hydrophobic kaolin hollow fiber membranes (h-KHFM) were used through phase inversion/sintering technique [109], and then it was followed by grafting with fluoroalkylsilane (FAS) molecules as a modification in which its ability for the simultaneous removal of arsenite and arsenate was investigated through direct contact membrane distillation (DCMD) system. Results showed that the wettability and strength properties of the membrane were enhanced by hydrophobization of KHFM into h-KHFM. Moreover, it has been revealed from the obtained results that preparing h-KHFM at a sintering temperature of 1300 °C induced an excellent liquid entry pressure (LEPw) value of 2 bar and high contact angle value of 145° as well as 0.32 μm average pore size. Consequently, at a feed temperature of 60 °C, the required standard of maximum contaminant level of arsenic was met, with 100% removal of both arsenite and arsenate with high permeate flux of 28 kg/m^{2}h and 25 kg/m^{2}h, respectively.

Manna and Pal [110] investigated arsenic removal from groundwater by utilizing solar energy for phase change in a new flash vaporization membrane distillation (FVMD) module, which was fitted with a composite flat-sheet PTFE membrane. This technique has more process safety and lower equipment cost when compared to nanofiltration and reverse osmosis as well as electrodialysis. Monitoring of both the membrane flux and rejection of arsenic has been done during variation of different parameters including feed temperature, distillate temperature, and velocity and the concentration of arsenic in the feed, as well as the operating hours. The results showed that, in all the investigated parameters, more than 99% rejection of arsenic with the highest flux of 52.94 kg/m^{2}h was achieved with the cross-flow mode of the FVMD module working in the configuration of direct contact membrane distillation (DCMD). Moreover, it has been observed that membrane performance in terms of arsenic rejection and flux remained the same after 40 h of investigation. The obtained results indicate the applicability of the solar-powered FVMD system for the removal of arsenic from groundwater. However, based on our knowledge, this treatment technique is still applicable on a small scale, and more detailed research is required to apply it on a larger scale taking into consideration the water flux, cost, and time consumed. Therefore, other treatment techniques could be used such as biological treatment methods.

Treatment of Groundwater by Electrocoagulation Method

The electrocoagulation process involves the use of metal cation as a coagulant, while iron or aluminum is used as an anode in an electrochemical reaction. As a result of this reaction, the metal anode is oxidized, while metal cation is released into the solution. This metal cation then reacts to form metal hydroxides resulting in the agglomeration of pollutants. Overall, in an electrocoagulation system, metals are removed through oxidation, reduction, co-precipitation, and adsorption mechanisms [111]. Ullah et al. [112] mentioned that the remediation mechanism of groundwater by zerovalent iron (ZVI) depends on the standard redox potential (E^0) as well as the metal ions' chemical speciation. Adsorption is used for remediation of metal contaminants with E^0 close to or more negative than that for Fe^0, while metal contaminants with much more positive E^0 value than Fe^0 are removed by surface-mediated reductive precipitation. On the other hand, both reduction and adsorption process could be used for the remediation of metallic cations such as Pb^{2+} and Ni^{2+} that are slightly more electropositive than Fe^0. According to Guan et al. [113], since Fe oxide/hydroxide precipitation is a dynamic process, contaminants in groundwater are removed either by adsorption where they are adsorbed into the aged Fe oxyhydroxides or

by precipitation where contaminants are adsorbed into the nascent Fe oxyhydroxides in which during aging they can be entrapped in their structure.

Maitlo et al. [114] investigated the use of iron-air fuel cell electrocoagulation (IAFCEC) system for the removal of chromium (Cr(VI)) from groundwater as an innovative and cost-effective treatment technique. The obtained results from this study illustrated the ability of this treatment option to remove 100% of chromate in groundwater within 4 h and 0.2 USD m^3 as operating cost. Since chromate is mobile in groundwater, it is suggested for the removal of chromate in electrocoagulation to have electrochemical oxidation of zerovalent iron to Fe(II) ions and reduction of Cr(VI) to Cr(III) ions at the surface of the anode and cathode electrodes, respectively. These reactions are usually accompanied by Cr(OH)$_3$ and Fe(OH)$_3$ co-precipitation inside the reactor. Moreover, the obtained results showed that the in situ production of stable iron hydroxides during IAFCEC operation leads to the co-precipitation of Cr(VI). It is evident from the merits of this system that it is less dependent on the initial pH, supporting electrolyte concentration, treatment capacity, and operating time. Thus, the IAFCEC can be recommended as one of the best options for the removal and treatment of chromium. According to the literature, the chromium remediation mechanism through electrocoagulation can be described in two ways: firstly, chromate in an aqueous medium interacts with Fr(II)- and Fe(II)-bearing minerals such as biotite and magnetite which in turn causes the chromate reduction into chromite ions. Then, inside the reactor, co-precipitation of Cr(OH)$_{3(s)}$ and/or (Fe, Cr)(OH)$_{3(s)}$ takes place. Secondly, inner-sphere monodentate and bidentate complexes form on the surface of aqueous chromate ions (HCrO$_4^-$ and CrO$_4^{2-}$) and iron oxides after their interaction [115, 116].

Similarly, Amarine et al. [117] used electrocoagulation for the removal of nitrate and sulfate simultaneously from groundwater due to its simplicity, ease of operations, and cost-effectiveness as well as high efficiency (Table 6). The experiments were carried out in a batch cell with aluminum electrodes. Results showed that the removal efficiency for nitrate reached up to 94.1%, while sulfate removal efficiency reached up to 97.86%.

Figure 2 a describes the simultaneous removal of Mn^{2+}, Fe^{2+}, and antibiotics in groundwater using peroxymonosulfate (PMS)–assisted in situ oxidation/coagulation (O/C) coupled with ceramic membrane process [118]. Here, the $^•$OH and SO$_4^{•-}$ will be generated in situ during the oxidation process through the activation of PMS by ferrous within groundwater, and precipitate ferric hydroxides or manganese during the coagulation process. Guo et al. [119] studied the simultaneous removal of NH$_4^+$ and Mn^{2+} from groundwater using iron-manganese co-oxide filter film (MeOx) as a catalyst. NH^{4+} was oxidized to NO^{3-} through the process of catalytic oxidation (Fig. 2b). Yang et al. [120] studied the simultaneous

removal of Cs$^+$ and Sr^{2+} from groundwater using low-cost inorganic ion exchange materials such as sulfur-modified chabazite (CHA). It was concluded that the selectivity of Cs$^+$ was enhanced by the sulfur loading. This was due to the increase of the Lewis acid-base interaction between sulfur and Cs$^+$. However, as the sulfur loading increased up to 5%, there was a slight increase in the selectivity of Sr^{2+} and decreased subsequently (Fig. 2c).

Treatment of Groundwater by Biological Treatment Methods

Biological treatment refers to the use of microorganisms, algae, and fungi for the degradation/removal of pollutants from water under aerobic and anaerobic conditions. Biological agents remove pollutants in a variety of ways. The organic pollutants are removed through oxidation or incorporation into the living cells or through utilizing them as a source of carbon and energy [121], whereas some inorganic pollutants are removed through secondary mechanisms such as by the production of extracellular polymeric substances like polysaccharides and proteins. These substances are able to produce complexes with metal ions, thereby removing them from the aqueous medium [122]. Moreover, microorganisms have the capabilities to withstand the high toxicity of these metals and can also remediate these metals through a variety of metabolic processes resulting in oxidation and reduction of these metals [123]. Biological treatment techniques are cost-effective as they use microbial degradation, adsorption by microbial biomass (living or dead), and bioremediation technologies. Biological techniques are being utilized in conjunction with other techniques to improve the sustainability and cost-effectiveness of these techniques. There are a variety of biological techniques that have been used for the removal of metals such as biological aerated filters (BAF), anaerobic suspended growth biological reactors, sequencing batch reactors (SBR), phytoremediation, anaerobic sequencing batch reactor (ASBR), and microbial fuel cells (MFCs).

Crognale et al. [124] evaluated the potential of treating arsenic-contaminated groundwater by biological As(III) oxidation in biofilters by establishing biofilms from native groundwater microorganisms. The 90% oxidation efficiencies were reached within 3 h with an initial arsenic concentration of 0.1 mg/L by using coarse sand biofilters. Furthermore, detailed microbial characterization of As(III) oxidizing biofilms was carried out and indicated the presence of various OTUs affiliated with different families that are known for their oxidizing ability for As(III), namely *Burkholderiaceae*, *Comamonadaceae*, *Rhodobacteraceae*, and *Xanthomonadaceae*. To sum up, the obtained results indicate the high potential of the biological As(III) oxidation process in biofilters with filling material that has low cost and easily availability. Moreover, the native

Table 6 Summary of the removal efficiencies of different removal techniques discussed in the paper for the removal of different contaminants from groundwater

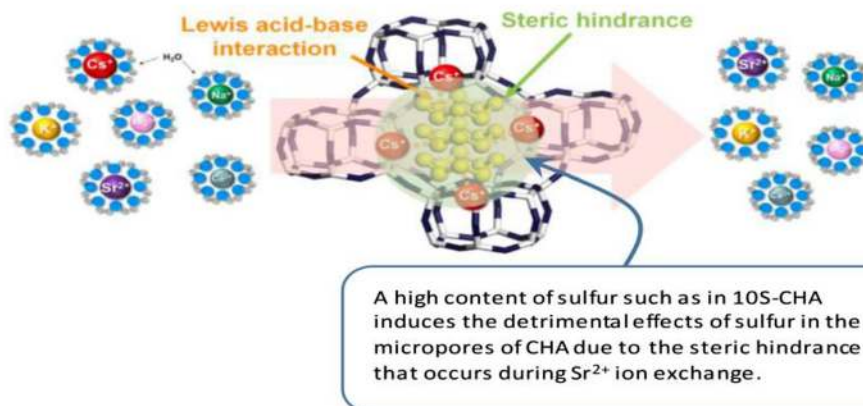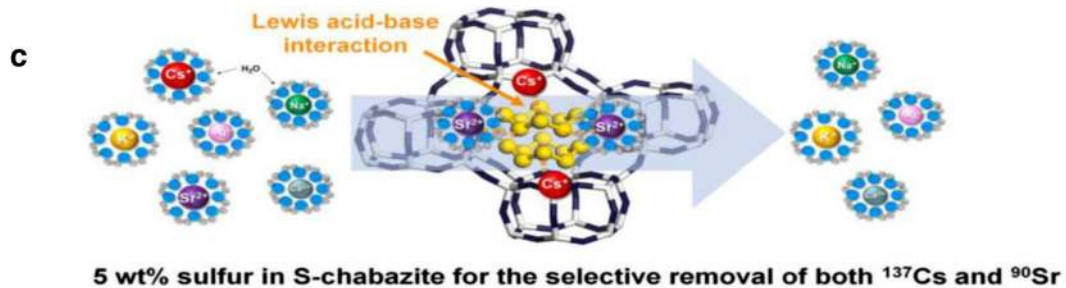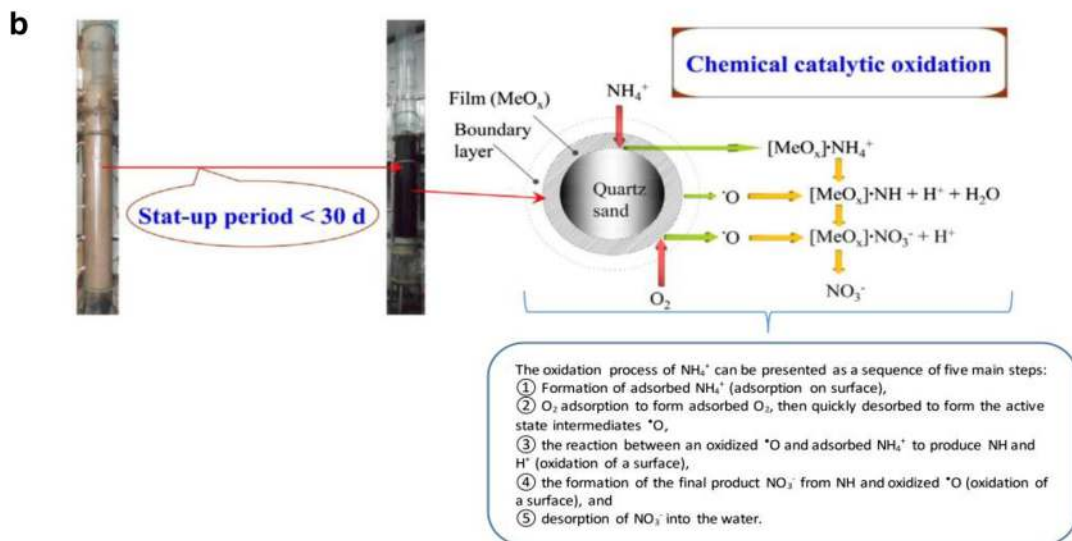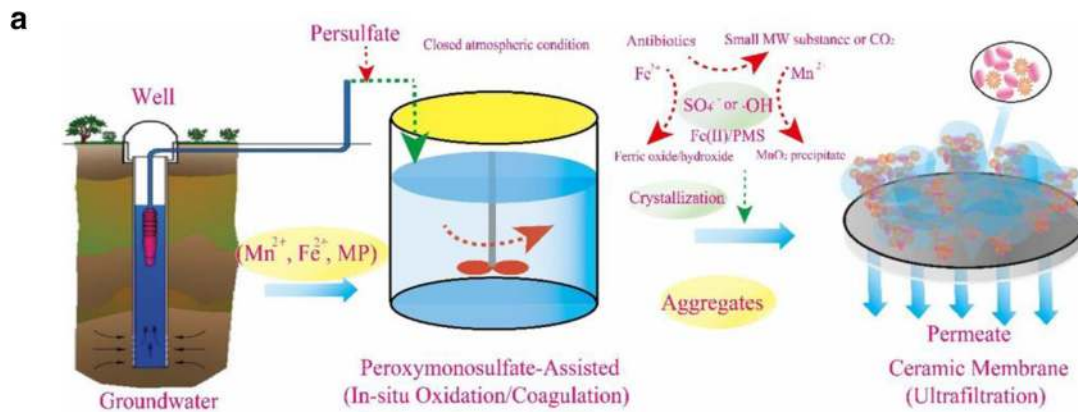| No.	Contaminant	Removal technique	Removal efficiency (%)	Reference
1	Arsenic	Solar-powered flash vaporization membrane distillation	99.0	[110]
		Iron oxide–coated sand column filter	99.0	[39]
		Natural/synthesized magnetic material by humic acid and *Bacillus pasteurii*	90–100	[37]
		Biofilters	90.0	[124]
2	Boron	Magnetic magnetite nanoparticles	90.0	[51]
3	Cesium	Microwave-based regenerating permeable reactive barrier	80.0	[30]
4	Chromium	Iron-air fuel cell electrocoagulation	100.0	[100]
5	Chromium	Nanoscale zerovalent iron-permeable reactive barrier	89.7	[101]
6	Copper and cadmium	Coated sand-humic acid	98.0	[102]
7	Fluoride	Calcinated sludge	70.0	[62]
		Multi-functional 3-layered Ag-MgO/nanohydroxyapatite composite	90.0	[63••]
8	Iron and manganese	Advanced magnetic hydroxyapatite nanocomposite	95–98	[96]
9	Lead	*Moringa oleifera* seeds and *Musa cavendish* peel	81.0	[130•]
10	Lead, cadmium, zinc	Lime softening waste on cement-based filter media	100.0	[97]
11	Nitrate and sulfate	Electrocoagulation	94.1–97.86	[117]
12	Nitrate, magnesium, phosphorus, and zinc	*Scenedesmus* sp. immobilized on alginate gel	92–100	[133]
13	Nitrogen	Raw straw-permeable reactive barrier	> 60	[103]
14	Vanadium	Sawdust pine-carbon source for microbial removal	82.60	[135]

groundwater bacteria had the ability to tolerate high concentrations of arsenic and can easily form highly As(III) oxidizing biofilms.

Shakya and Ghosh [125] demonstrated the removal of nitrate, arsenic, and iron from contaminated groundwater in an anaerobic suspended growth reactor system (SmBR) inoculated with a mixed indigenous bacterial culture. Results showed that the SmBR was able to simultaneously remove nitrate, arsenic, and iron present at different concentrations from real groundwater to levels below the permissible drinking water limits after the addition of sulfate insufficient amount. Furthermore, iron was removed from groundwater through the formation of iron sulfides by the presence of biogenic sulfides, while the main arsenic removal mechanism was through the precipitation of arsenosulfides, co-precipitation, and/or adsorption on iron sulfides.

Moreover, Zhang et al. [126] investigated the biotransformation mechanism of chromium Cr(VI) as well as the biogeochemical fate of the reduced chromium in groundwater by studying the sulfur-based mixotrophic bio-reduction where Cr(VI) is the only electron acceptor and organics and elemental sulfur as co-donors of electrons. This study demonstrates the effectiveness of this process in the detoxification process of Cr(VI) in which 95.5% removal efficiency was achieved within 48 h at 50 mg/L as the initial concentration; these

results were higher than the removal efficiency achieved by autotrophic and heterotrophic reductions combined. This process can be implemented for the in situ Cr(VI) bioremediation in groundwater. Similarly, Panousi et al. [127] studied the removal of Cr(VI) from highly contaminated groundwater by sequencing batch reactors (SBR) operating under anaerobic conditions where the main electron acceptor was sulfate as well as under anoxic conditions where nitrate was the main electron acceptor. Results showed that the complete reduction of Cr(VI) to Cr(III) under an initial Cr(VI) concentration of 1.8 ppm was supported by the anaerobic conditions of the SBR system. On the other hand, complete removal of Cr(VI) was achieved under anoxic conditions and Cr(VI) initial concentration of 10 ppm. However, increasing the initial concentration caused a decrease in the removal efficiency under anaerobic conditions. Based on the maximum specific growth

Fig. 2 **a** Schematic of the simultaneous removal of Mn^{2+}, Fe^{2+}, and ▶ antibiotics in groundwater using peroxymonosulfate (PMS)–assisted in situ oxidation/coagulation (O/C) coupled with ceramic membrane process [118]. **b** Simultaneous removal of NH_4^+ and Mn^{2+} from groundwater using iron-manganese co-oxide filter film (MeOx) as a catalyst [119]. **c** Simultaneous removal of Cs^+ and Sr^{2+} from groundwater using low-cost inorganic ion exchange materials such as sulfur-modified chabazite (CHA) [120]

a

Peroxymonosulfate-Assisted
(In-situ Oxidation/Coagulation)

Permeate
Ceramic Membrane
(Ultrafiltration)

b

Chemical catalytic oxidation

$[MeO_x] \cdot NH_4^+$

$[MeO_x] \cdot NH + H^+ + H_2O$

$[MeO_x] \cdot NO_3^- + H^+$

NO_3^-

The oxidation process of NH_4^+ can be presented as a sequence of five main steps:
① Formation of adsorbed NH_4^+ (adsorption on surface),
② O_2 adsorption to form adsorbed O_2, then quickly desorbed to form the active state intermediates $^\bullet O$,
③ the reaction between an oxidized $^\bullet O$ and adsorbed NH_4^+ to produce NH and H^+ (oxidation of a surface),
④ the formation of the final product NO_3^- from NH and oxidized $^\bullet O$ (oxidation of a surface), and
⑤ desorption of NO_3^- into the water.

c

5 wt% sulfur in S-chabazite for the selective removal of both ^{137}Cs and ^{90}Sr

A high content of sulfur such as in 10S-CHA induces the detrimental effects of sulfur in the micropores of CHA due to the steric hindrance that occurs during Sr^{2+} ion exchange.

rates, the acclimatized biomass under anaerobic conditions had a much lower tolerance of Cr(VI) when compared with the acclimatized biomass under anoxic conditions.

da Conceicao et al. [128] investigated the fluoride reduction in groundwater by using coagulation with *Moringa oleifera* Lam seeds combined with microfiltration. The experiments were performed in a jar test with various coagulant concentrations and then, groundwater was subsequently treated with microfiltration membranes. The results showed that with an initial fluoride concentration of 5 mg/L and 5 g/L of the *Moringa oleifera* coagulant the obtained treated water had a fluoride residual (1.2 mg/L) that meets the recommendations of the WHO. Therefore, it is indicated that the combined process of natural and biodegradable coagulant with the microfiltration process provides an alternative treatment for the removal of excessive fluoride from groundwater.

For the removal of molybdenum from groundwater, Carnevale et al. [129] reported the application of brown seaweed (*Petalonia fascia*) as an adsorbent. The experiments were performed in batch and continuous systems and results showed that the highest adsorption capacity was 1376 mg/g. The high adsorption capacity and low cost of the adsorbent make it a good alternative to be used in the treatment of groundwater from molybdate anions. Aziz et al. [130•], on the other hand, determined the use of *Moringa oleifera* seeds and *Musa cavendish* peel as low-cost plant-based biomass for the simultaneous removal of nickel, lead, and cadmium ions from groundwater. The used plant-based biomass was pretreated by HNO_3 and then by NaOH for the enhancement of its treatment efficiency. Results indicated the efficiency of the used biomass in the removal of the tested heavy metals due to the presence of various functional groups, which were playing the main role in the removal mechanism, namely C-C, C=O, and N-H. Results showed that increasing the initial concentration of lead ions increased the removal efficiency by *Moringa oleifera* seed from 65 to 81% and a similar trend was observed when both biomass (*Moringa oleifera* + *Musa cavendish*) were used for the adsorption of lead ions. However, nickel removal by *Moringa oleifera* decreased with increasing the initial nickel concentration. On the other hand, higher removal efficiency was observed when using *Moringa oleifera* + *Musa cavendish* at a high initial concentration of nickel or cadmium when compared to the use of a single adsorbent. Furthermore, $17 was the total cost for the treatment of 50 L groundwater, which proves the suitability of this treatment technique for communities with lower income.

Al-Mamun et al. [131] presented the feasibility of continuous up-flow baffled microbial fuel cells (MFCs) with carbon brush electrodes for the oxidization of organics present in the sewage by the exoelectrogens on the anode producing electricity and simultaneously removal of nitrogen from groundwater by using the generated electricity. Anaerobic sequencing batch reactor (ASBR) was integrated before the MFCs to remove nitrogen from groundwater. It was revealed that the integration of ASBR with the biocathode increased the nitrogen removal from groundwater by 136% that is higher than the removal without the ASBR system. The obtained results indicate the efficiency of using the ASBR system as pretreatment and using the solubilized organics successively in denitrifying biocathode MFC for the simultaneous recovery of energy as well as nitrogen removal from groundwater. Similarly, the removal of NH_4^+-N, NO_2^--N, and NO_3^--N from groundwater was achieved through adsorption by the composite active medium of nitrogen-degrading bacteria immobilized consortia [132]. The ability of the composite active medium to remove nitrogen was found to be significantly enhanced by the immobilization of the degrading bacteria on scoria in comparison with the use of scoria alone. *Pseudomonas*, *Stenotrophomonas*, and *Serratia* were found to be the best bacterial genera for effective removal of nitrogen in its three tested forms.

Mollamohammada et al. [133] determined the capability of using *Scenedesmus* sp. immobilized on alginate gel for the simultaneous removal of nitrate, magnesium, phosphorus, and zinc from groundwater in a continuous flow reactor (Table 6). Results showed that immobilized *Scenedesmus* sp. beads were able to simultaneously remove 92%, 100%, 99.9%, and 92% of nitrate, magnesium, phosphorus, and zinc from groundwater after 29 days, respectively. Zhou et al. [134] identified the effect of sulfate on the simultaneous removal of nitrate and selenate from groundwater by a hydrogen-based membrane biofilm reactor (MBfR). Results showed that sulfate had no obvious effect on the removal of both selenate and nitrate as almost 100% removal efficiency was achieved. Furthermore, the microbial ecology indicated that the stable and efficient degradation of nitrate was achieved by *Hydrogenophaga* as one of the contributors, while *Desulfovibrionaceae* promoted the degradation of selenate. However, other microorganisms that exist in groundwater are considered a source of contamination.

The bioremediation of vanadium from groundwater was also done by sawdust pine as a carbon source and anaerobic sludge as inocula [135]. The 90.3% removal efficiency was achieved in nutrient solution and the accumulation of microbes such as *Thauera* could contribute to the reduction of vanadium. The reduction of vanadium was mediated by the microbes' synergistic interactions. Furthermore, in real groundwater; the vanadium removal could be increased from 53.2 to 82.6% by adding phosphate rock and medical stone.

Removal of Microorganisms from Groundwater

The presence of pathogens (bacteria, viruses, and protozoa) in groundwater is a worldwide concern for public health. Many

studies have shown the presence of a variety of pathogens in groundwater that have been associated with different disease outbreaks [136]. These outbreaks can be detected by linking the information related to the increase in illness in the population exposed to the presence of pathogens in the water consumed. However, in routine practice, many outbreaks caused by contaminated water remain unrecognized, as it is difficult to link the increase in illness to the presence of causative agents in water. Moreover, the detection of pathogens in water samples is also more complicated as compared to biological samples [137]. Commonly found pathogens in water are *Cryptosporidium parvum*, *Giardia intestinalis*, *Campylobacter jejuni*, norovirus, and others [138, 139••].

Generally, there are various techniques that have been used for the removal of pathogens from water, such as sand filtration, disinfection (UF, ozone, chorine), adsorption, filtration, and activated sludge systems, which are discussed below. For example, Andreoli and Sabogal-Paz [140] investigated the performance of two different settings of household slow sand filters HSSF, namely intermittent (I-HSSF) and continuous (C-HSSF) flow that are followed by sodium hypochlorite for disinfection to simultaneously remove *Escherichia coli*, *Giardia muris* cysts, and *Cryptosporidium parvum* oocysts from groundwater. Two operation phases were evaluated in this study to accelerate the HSSF ripening, with and without the use of river water as a ripening agent. A ripening agent usually is introduced to the filter to provide nutrients for the development of the biological layer in a short time. Results showed that better removal efficiency of microbes in groundwater was achieved by C-HSSF when compared to I-HSSF. Furthermore, it was observed that the weekly feeding of HSSFs with river water as a ripening agent sped up the ripening process in around 80 days, which in turn lead to treatment efficiency improvement compared to the operation without the ripening agent. The obtained results indicated the applicability of HSSF in rural communities to provide safe water.

Alvear-Daza et al. [141••] evaluated the simultaneous removal of *Escherichia coli* and *Klebsiella pneumoniae* from groundwater by coupled helio-photochemical processes with artificial UVB + UVA + visible light in the presence of H_2O_2 with rapid sand filtration and chlorination step. Results indicated that several natural photo-induced processes such as photocatalytic and photo-Fenton could be enhanced by the simple attrition of H_2O_2 and natural sunlight as well as artificial light irradiation, as the total reduction of *Escherichia coli* and *Klebsiella pneumoniae* could be due to such radicals. To remove pathogenic bacteria from groundwater, Mpenyana-Monyatsi et al. [142] developed low-cost filter materials coated with silver nanoparticles that were deposited on zeolite, sand, fiberglass, and anion and cation resin substrates in different concentrations for the simultaneous removal of pathogens from groundwater. Results showed that using Ag/cation resin achieved 100% removal efficiency of *E. coli*,

S. typhimurium, *S. dysenteriae*, and *V. cholerae*, while other filters had lower removal efficiency in the range of 8 to 67%. The obtained results suggested the use of Ag/cation resin as a disinfection technique for groundwater.

Adsorption technique, as a cost-effective technology, has been used for the removal of pathogenic microorganisms from water. For example, Chung et al. [143] determined the simultaneous removal of pathogenic rotavirus and adenovirus from groundwater by hydrochar derived from sewage sludge amended sand beds as an adsorbent. Results showed that more than 99% removal efficiency was achieved that is corresponding to 2.4-log removal of both viruses by the used adsorbent. The introduction of hydrophobic and/or meso-/macro-surface structure of the hydrochar could be responsible for the improved removal efficiency in which it provided favorable attachment sites for rotavirus and adenovirus. Obijole et al. [144] prepared hydrothermally treated aluminosilicate clay for the simultaneous removal of fluoride and bacteria from water. The prepared adsorbent had an adsorption capacity of 1.75 mg/g for fluoride ions and removed 53% of fluoride from water. Moreover, the efficiency of the prepared materials was noted against *E. coli* in terms of zone of inhibition for bacterial growth.

Some researchers have also applied nanocomposites for the successful removal of pathogenic microorganisms from water. Ayinde et al. [145] combined microwave and ultrasonically modified methods as a greenway for the synthesis of multifunctional Ag-MgOHap nanocomposite. The impregnation of the reduced Ag and MgO nanoparticles on the adsorbent surface occurred by *Citrus paradisi* peel extract to evaluate its antimicrobial activity against *Escherichia coli* and *Klebsiella pneumonia* in groundwater. Results indicated that the synthesized nanocomposite has a strong and effective antibacterial activity towards *Escherichia coli* and *Klebsiella pneumonia*. It was shown that *Escherichia coli* were more susceptible than *Klebsiella pneumonia* with an inhibition zone of 13 mm and 10 mm, respectively. The antimicrobial activity of the nanocomposite and the death of the cell membrane for the microbes could be attributed to the penetration of both Ag and MgO ions that were released from the nanoparticles on the adsorbent surface as well as their interaction with the bacterial genome and other cellular enzymes. Ayinde et al. [63••] also investigated the green synthesis of metal-metal oxide nanoparticles supported on chitosan matrix (AgMgO/nHaP@CSn) for the simultaneous removal of pathogens from groundwater. Results showed that the inhibition zone for gram-positive *Staphylococcus aureus* was higher than that for gram-negative *Escherichia coli*. The AgMgO/nHaP@CSn nanocomposite mechanism could be due to the inherent synergistic antibacterial activity of these nanomaterials. These synergistic properties include the wide contact interaction because of the larger surface area as well as the surface charges

between the nanocomposite and the bacterial cell wall. These results indicate the nanocomposite potential to treat groundwater contaminated with pathogens. Similarly, Sivaselvam et al. [146] prepared MgO nanostructures of variable shapes (spherical and cubicle) to test their antibacterial activity in water. It was noted that both nanostructures were able to inhibit bacterial growth by inducing intracellular production of reactive oxygen species (ROS) and by physically damaging the surface of the bacterial cell.

Magnetic nanoparticles (MNPs) have also gained significant attention owing to their superior properties and characteristics. However, grafting these magnetic nanoparticles with amino functional groups has further improved their performances against a variety of pollutants including heavy metals, microorganisms, and other organic pollutants in water [146]. The antibacterial activities of green synthesized iron nanoparticles (FeNPs) using leaf and seed extract of *Moringa oleifera* (*M. oleifera*) were tested against *Escherichia coli* (*E. coli*) [147]. The antibacterial activity results showed that *M. oleifera* leaf is less resistant to *E. coli* as it had an inhibition zone of 5 mm, while *M. oleifera* seed was more resistant with an inhibition zone of 6 mm. The positively charged Fe ion may be the reason for the antibacterial activity through the attraction between the microorganisms' negatively charged cell membrane.

Advancement of Sorbents for Various Pollutants Through Material Design

This section mainly discusses and explores the rational material design to combine the interaction mechanisms for the simultaneous removal of various contaminants such as heavy metals as shown in Fig. 3. Graphene-based sorbents are used as model sorbents as they can be designed in different ways such as shaping them into various forms like hydrogels, aerogels, fluids, powder, and particles; optimizing their textural properties and their chemical functionality can be tailored for various treatment applications. Moreover, the binding tendency of charged pollutants such as heavy metal ions towards the graphene surface can be increased because of the generated surface charge on the graphene surface as well as its counterparts through the heteroatom doping and functionalization. Groups containing oxygen, nitrogen, and sulfur are commonly introduced to the framework of graphene in which the grafting process can be achieved through thermal annealing, plasma treatments, wet chemical methods, microwave synthesis, hydrothermal, and solvothermal [148, 149]. Modification strategies including heteroatom doping (such as phosphorus, nitrogen, boron, and sulfur) and chemical functionalization that can be applied to graphene-based sorbents can enhance its adsorption performance in the removal process of pollutants from water. This is due to the challenges faced by the synthesis of graphene-based sorbents as it is still

Fig. 3 Various interaction types involved in the adsorption of heavy metals onto graphene-based sorbent [155]

Adsorption of heavy metal ions on graphene oxide through surface complexation
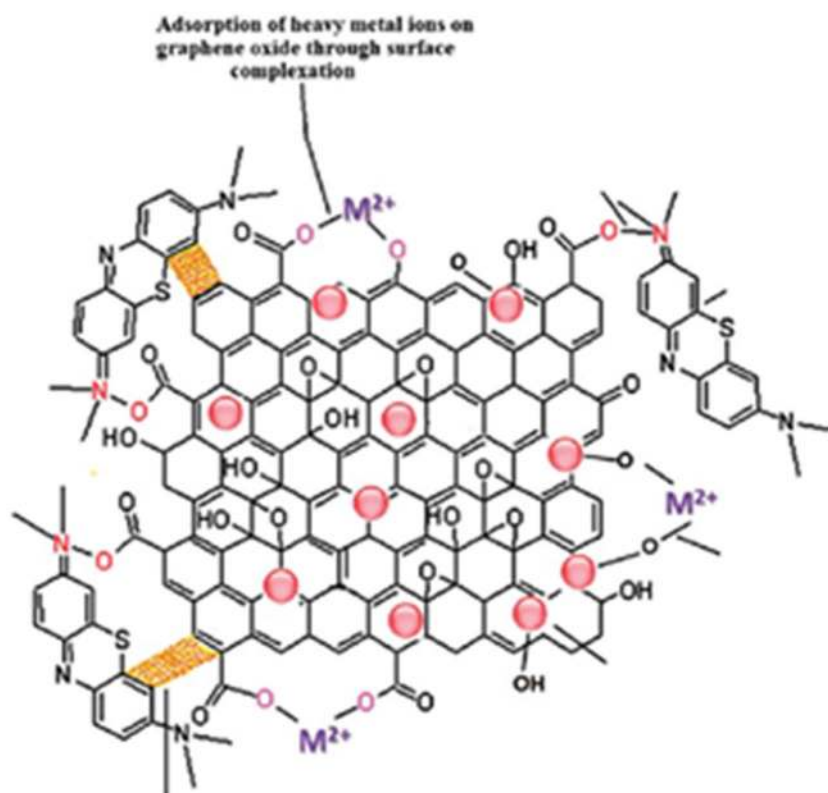
limited by the chemical inertness, high hydrophobicity, low water dispersion, and its tendency to undergo π- π stacking [150]. The cost of applying the advanced graphene sorbent is a barrier that limits its application. However, the treatment cost should take into consideration the treatment time, performance efficiency, and regeneration feasibility to achieve a sustainable water treatment technology. Since using graphene-based adsorbents has a high regeneration rate, high-performance efficiency, and only a small amount of it is required to treat large volumes of polluted groundwater, it can be considered a promising economically feasible treatment process in comparison to other commercial sorbents like activated carbon [151].

Pan et al. [152] investigated the simultaneous removal of lead, copper, and cadmium from groundwater by fabricating a porous calcium alginate/graphene oxide composite aerogel by utilizing polystyrene colloidal particles as a sacrificial template and graphene oxide as a reinforcing filler to achieve high adsorption capacity. Results showed the removal rates of 95.4%, 81.2%, and 73.2, for lead, copper, and cadmium, respectively. It has been indicated by the analysis of the adsorption mechanism that the adsorption process occurred mainly through chemical coordination effects and ion exchange. Zare-Dorabei et al. [153] synthesized graphene oxide that is chemically modified with 2,2′-dipyridylamine (GO-DPA) for the simultaneous removal of lead, cadmium, nickel, and copper from groundwater. Results showed that the maximum adsorption capacities achieved were 369.7 mg/g, 257.2 mg/g, 180.9 mg/g, and 358.2 mg/g for lead, cadmium, nickel, and copper ions, respectively. Furthermore, chemical modification of graphene oxide with 3-aminopyrazole (GO-f) was synthesized for the simultaneous removal of cadmium, mercury, and arsenic from groundwater due to the important role played by the nitrogen-containing functional groups existing on the surface of the adsorbent [154]. Results showed that the adsorption affinity order was cadmium > mercury > arsenic with an adsorption capacity of 285.7 mg/g, 227.3 mg/g, and 131.6 mg/g, respectively. The obtained results could be attributed to the presence of functional moieties and hydrophilic character as well as the high surface area of GO-f. Pirveysian and Ghiaci [155] used Na$_2$S as a functionalizing precursor in developing sulfur functionalized graphene oxide (GO-SO$_x$R) sorbent for the simultaneous removal of lead, cadmium, nickel, and zinc, in which outstanding maximum adsorption capacities of 285 mg/g, 217 mg/g, 175 mg/g, and 196 mg/g were obtained for the investigated metals, respectively. Moreover, in this study, GO-SO$_x$R was coated with TiO$_2$ and SiO$_2$ to improve the sorbent adsorption capacity. Results showed that SiO$_2$ improved the removal rate of cadmium only, while TiO$_2$ showed higher adsorption capacities for all heavy metals as it increased to 312 mg/g, 384 mg/g, 344 mg/g, and 285 mg/g, for lead, cadmium, nickel, and zinc, respectively.

Practical Implications and Challenges of Groundwater Treatment

The effective management of groundwater requires attention for securing the water requirements of agricultural and industrial activities. This paper reviews the cost-efficient treatment techniques for the simultaneous removal of multi-elements and microorganisms from groundwater and the removal mechanisms of certain contaminants by using specific treatment techniques, as well as the challenges and cost analysis of groundwater treatment. However, there are various challenges that face the application of economic instruments for the treatment of groundwater such as (i) time lags of contaminants as they take a long time before reaching the aquifer, causing difficulty in monitoring the effectiveness of the protection measures. Furthermore, the variability of the time lags depends on several factors, namely precipitation, soil type, or saturation. (ii) Hydrogeological conditions of the contaminated site determine the impact of the contaminant; such conditions include topsoil layer, soil type, aquifer's depth, and volume, as well as its connections to surface water bodies; and (iii) prediction of the location-specific economic shifts that occur due to the rise in water prices as well as finding ways to reduce it [156].

For instance, the ion exchange technique is a promising technique for the treatment of water with no generation of sludge, but this process is limited to specific pollutants as well as requires a high cost for the replacement of the resin over time. Although the membrane filtration process is efficient in water treatment and can have high removal capacities without the generation of secondary pollution, its high manufacturing costs, severe fouling, and high-energy consumption are major drawbacks that limit its application. It is also strongly indicated that adsorption is considered an efficient treatment technique for the removal of various contaminants from groundwater by utilizing different adsorbents. However, prior to the implementation of the adsorption process for the treatment of groundwater, the cost of adsorbent regeneration should be considered, as some regeneration processes are energy-intensive and costly. In such cases, other treatment options should be investigated such as biological treatment techniques. Treating groundwater in a biological treatment system can greatly influence the requirements and cost of disposing of spent adsorbents and sludge, which will contain metals and other pollutants.

Furthermore, the cost of the treatment depends on the quality of groundwater as, if it has good quality, several treatment processes will be neglected which in turn reduces the treatment cost. On the other hand, the treatment cost will increase when the water has a very low quality due to the increased chemical usage. Moreover, cost analysis has a significant variation between different contamination sites, and various factors that could impact the treatment cost are site-specific

[157]. Figure 4 summarizes how to determine the best treatment option [158, 159]. According to Reddy [159], the characterization of the contamination site before assessing the hazardous risk is of utmost importance as the characterization includes defining the site's geology, hydrology, and contamination, locations, and demographics of the nearby populations, as well as the potential releases to the environment. After that, a hazardous risk assessment for the contaminated site can be performed and the appropriate treatment action can be selected. Treating specific contamination requires the understanding of subsurface conditions as well as the advantages and disadvantages of each treatment technique that can be used. This is important to avoid making the contamination site worse by choosing and implementing improper treatment techniques. Since there are various treatment technologies for groundwater remediation, for choosing the best

treatment option in terms of economic and effective treatment, five strategies for the assessment of treatment techniques are proposed [160]:

1. Understanding the requirements of the treatment as well as the implications of water quality comparing the quality of raw water with the goal of the treatment for the determination of the suitable treatment requirements and processes.
2. Choosing the optimal treatment technology, knowing the advantages and disadvantages of each treatment process, helps in determining which treatment to be used for specific contaminated groundwater. Some techniques are capable of removing several contaminants while others can only remove a few target pollutants.
3. Pretreatment processes might be needed to increase treatment efficiency.

Fig. 4 Summary of steps required for choosing the appropriate groundwater treatment technique
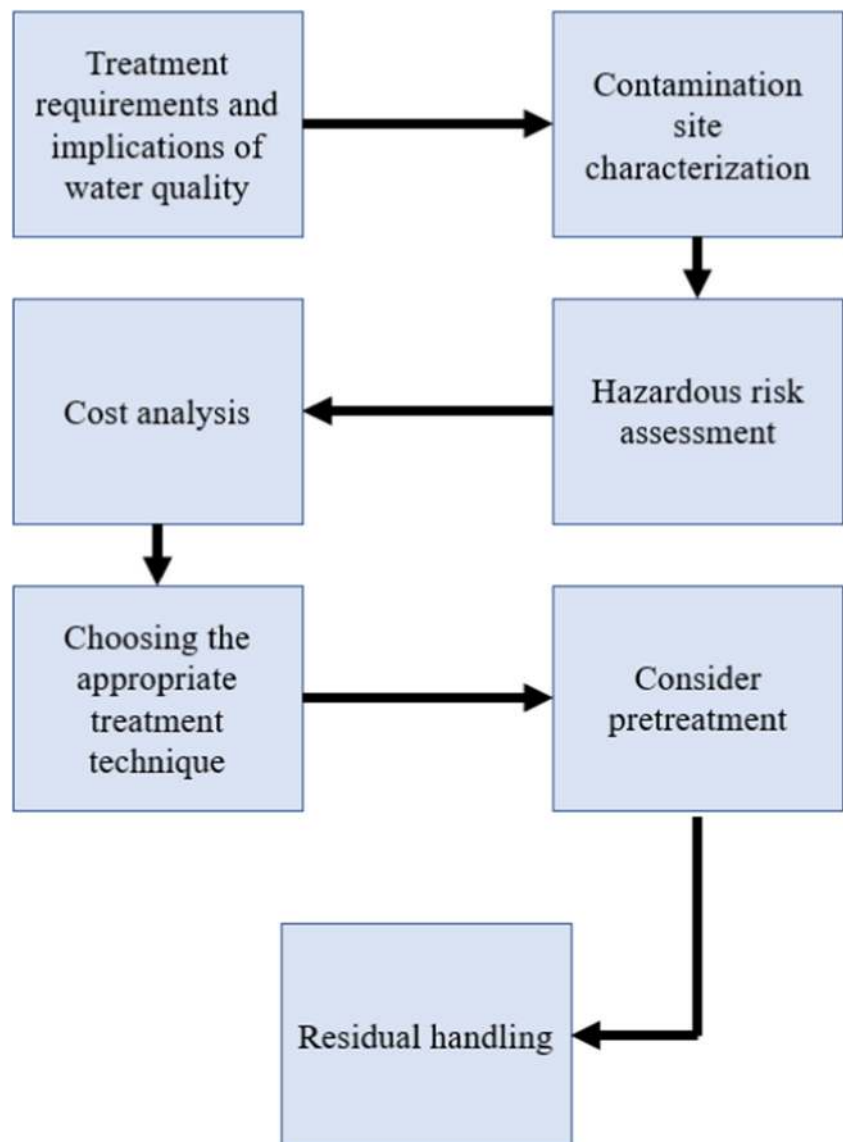
4. Handling the residuals, the residual handling requirements differ depending on the used treatment technology. For example, the adsorption process requires the replacement of the used media and some rinse to sewer, while biological filtration requires waste backwashing.
5. Biological filtration is a cost-effective process that does not demand high-energy consumption. It can remove different contaminants without multiple add-on unit processes.

Currently, the development of accurate comparison for the cost of treatment technologies is difficult due to various significant problems. Firstly, extrapolation of the reported costs under specific conditions at one site to other sites is very difficult. This can be attributed to the sensitivity of technology costs towards site-specific geological, geochemical, and contaminant conditions. Secondly, costs could be reported in various metrics that cannot be directly compared, such as the achieved reduction in the concentration of contaminants, dollars per treated volume, or surface area treated. These differences in cost reporting metrics make a comparison between the costs of different technologies by utilizing previous data at different sites very difficult. Thirdly, usually variable costs are not reported, namely system design, equipment mobilization to the contaminated site, or modification for site conditions. Lastly is the inconsistency in the derived way of costs [161].

Conclusion

In conclusion, groundwater is considered one of the main sources for agricultural, industrial, and drinking purposes. Unfortunately, anthropogenic and natural contamination has degraded the quality of groundwater and limited its usage around the world. In the literature, various studies have reported the contamination of metals like lead, boron, and cadmium in groundwater. The presence of various pathogenic viruses and bacteria has also been reported in the groundwater. Hence, the monitoring and treatment of groundwater have become highly important for the protection of public health and the environment.

There are several treatment techniques for the removal of such contaminants from groundwater and their capabilities vary from one to another. However, some techniques have drawbacks in terms of high-energy demands and cost in-effectiveness. In this paper, various examples of low-cost treatment techniques for the removal of different metals and microorganisms and their removal mechanisms were discussed. The criteria for choosing the right treatment technique were also discussed such as characterization and hydrogeological aspects of the contaminated site, hazardous risk assessment, the goal of the treatment (i.e., reuse options), and cost-benefit analysis. Finally, it is recommended that future research

should aim to understand the transport and fate of various emerging contaminants (metals, pathogens, and others) and should target to evaluate the treatment techniques for the removal of such water contaminants. Additionally, scientists from different disciplines (microbiologists, environmental engineers, and material scientists) should work together to develop water remediation techniques that can ensure the protection of natural water resources and public health and safety.

Compliance with Ethical Standards

Conflict of Interest On behalf of all authors, the corresponding author states that there is no conflict of interest.

Human and Animal Rights and Informed Consent This article does not contain any studies with human or animal subjects performed by any of the authors.

Disclaimer The findings achieved herein are solely the responsibility of the author(s).

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