



Review

**Arsenic removal from water/wastewater using
adsorbents—A critical review**Dinesh Mohan^{a,b,*}, Charles U. Pittman Jr.^a^a *Department of Chemistry, Mississippi State University, Mississippi State, MS 39762, USA*^b *Environmental Chemistry Division, Industrial Toxicology Research Centre, Post Box No. 80,
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Abstract

Arsenic's history in science, medicine and technology has been overshadowed by its notoriety as a poison in homicides. Arsenic is viewed as being synonymous with toxicity. Dangerous arsenic concentrations in natural waters is now a worldwide problem and often referred to as a 20th–21st century calamity. High arsenic concentrations have been reported recently from the USA, China, Chile, Bangladesh, Taiwan, Mexico, Argentina, Poland, Canada, Hungary, Japan and India. Among 21 countries in different parts of the world affected by groundwater arsenic contamination, the largest population at risk is in Bangladesh followed by West Bengal in India. Existing overviews of arsenic removal include technologies that have traditionally been used (oxidation, precipitation/coagulation/membrane separation) with far less attention paid to adsorption. No previous review is available where readers can get an overview of the sorption capacities of both available and developed sorbents used for arsenic remediation together with the traditional remediation methods. We have incorporated most of the valuable available literature on arsenic remediation by adsorption (~600 references). Existing purification methods for drinking water; wastewater; industrial effluents, and technological solutions for arsenic have been listed. Arsenic sorption by commercially available carbons and other low-cost adsorbents are surveyed and critically reviewed and their sorption efficiencies are compared. Arsenic adsorption behavior in presence of other impurities has been discussed. Some commercially available adsorbents are also surveyed. An extensive table summarizes the sorption capacities of various adsorbents. Some low-cost adsorbents are superior including treated slags, carbons developed from agricultural waste (char carbons and coconut husk carbons), biosorbents (immobilized biomass, orange juice residue), goethite and some commercial adsorbents, which include resins, gels, silica, treated silica tested for arsenic removal come out to be superior. Immobilized biomass adsorbents offered outstanding performances. Desorption of arsenic followed by regeneration of sorbents has been discussed. Strong acids and bases seem to be the best desorbing agents to produce arsenic concentrates. Arsenic concentrate treatment and disposal obtained is briefly addressed. This issue is very important but much less discussed.

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1. Introduction

Arsenic (atomic number 33) is ubiquitous and ranks 20th in natural abundance, comprising about 0.00005% of the earth's crust, 14th in the seawater, and 12th in the human body [1]. Its concentration in most rocks ranges from 0.5 to 2.5 mg/kg, though higher concentrations are found in finer grained argillaceous sediments and phosphorites [1,2]. It is a silver-grey brittle crystalline solid with atomic weight 74.9; specific gravity 5.73, melting point 817 °C (at 28 atm), boiling point 613 °C and vapor pressure 1 mm Hg at 372 °C. Since its isolation in 1250 A.D. by Albertus Magnus [1], this element has been a continuous center of controversy.

Arsenic is mobilized by natural weathering reactions, biological activity, geochemical reactions, volcanic emissions and other anthropogenic activities. Soil erosion and leaching contribute to 612×10^8 and 2380×10^8 g/year of arsenic, respectively, in dissolved and suspended forms in the oceans [3]. Most environmental arsenic problems are the result of mobilization under natural conditions. However, mining activities, combustion of fossil fuels, use of arsenic pesticides, herbicides, and crop desiccants and use of arsenic additives to livestock feed create additional impacts.

Arsenic exists in the -3 , 0 , $+3$ and $+5$ oxidation states [4]. Environmental forms include arsenious acids (H_3AsO_3 , H_3AsO_3 , $\text{H}_3\text{AsO}_3^{2-}$), arsenic acids (H_3AsO_4 , H_3AsO_4^- , $\text{H}_3\text{AsO}_4^{2-}$), arsenites, arsenates, methylarsenic acid, dimethylarsinic acid, arsine, etc. Arsenic(III) is a hard acid and preferentially complexes with oxides and nitrogen. Conversely, arsenic(V) behaves like a soft acid, forming complexes with sulfides [5]. Inorganic forms of arsenic most often exist in water supplies [5]. Arsenic is uniquely sensitive to mobilization (pH 6.5–8.5) and under both oxidizing and reducing conditions among heavy metalloids [6]. Two forms are common in natural waters: arsenite (AsO_3^{3-}) and arsenate (AsO_4^{3-}), referred to as arsenic(III) and arsenic(V). Pentavalent (+5) or arsenate species are AsO_4^{3-} , HAsO_4^{2-} , H_2AsO_4^- while trivalent (+3) arsenites include $\text{As}(\text{OH})_3$, $\text{As}(\text{OH})_4^-$, $\text{AsO}_2\text{OH}^{2-}$ and AsO_3^{3-} . Pentavalent species predominate and are stable in oxygen rich aerobic environments. Trivalent arsenites predominate in moderately reducing anaerobic environments such as groundwater [7].

Redox potential (Eh) and pH control arsenic speciation. H_2AsO_4^- dominates at low pH (less than about pH 6.9) in oxidizing conditions. At higher pH, HAsO_4^{2-} is dominant (H_3AsO_4^0 and AsO_4^{3-} may be present in strong acid or base conditions, respectively). Under reducing conditions at $\text{pH} < \sim 9.2$, the uncharged H_3AsO_4^0 predominates (Fig. 1; [8]). Arsenic species predominating in various pH ranges have been discussed [9–11,541]. Deprotations of arsenious (H_3AsO_3) and arsenic (H_3AsO_4) acids under differing conditions are summarized in Fig. 2 from the respective pK_a values [12]. Estimation of arsenic levels were discussed in literature [536,537,550,552,559,561].

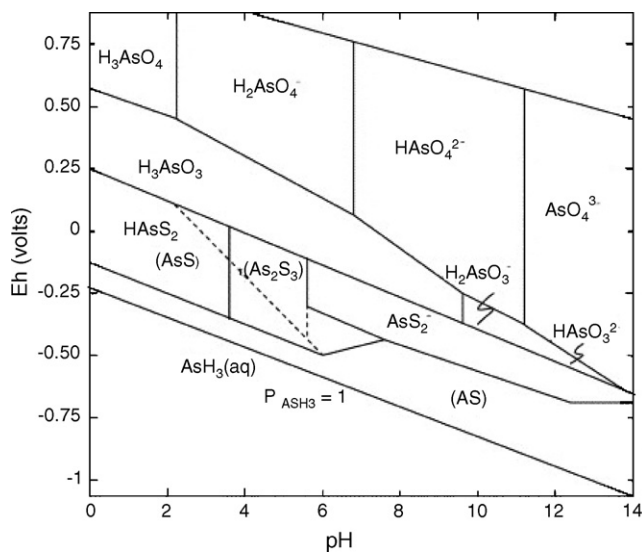


Fig. 1. The Eh–pH diagram for arsenic at 25 °C and 101.3 kPa (reprinted from [8] with permission from Elsevier).

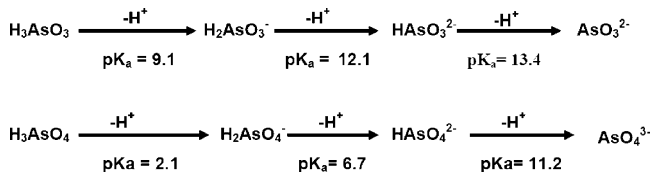


Fig. 2. Dissociation of As(V).

Table 1
Countries affected by arsenic contamination and maximum with permissible limits for drinking water

Country	Maximum permissible limits ($\mu\text{g/L}$)	References
Argentina	50	[4,406–410,540]
Bangladesh	50	[25,403,411–423]
Cambodia		[424]
China	50	[1,425–428,600]
Chile	50	[429–434,599]
India	10	[24,25,29,150,435–449]
Japan	–	[450]
Mexico	50	[23,163,451–454]
Nepal	50	[455]
New Zealand	10	[456–459]
Taiwan	10	[1,425,460–462]
USA	10	[22,32,33,463–469]
Vietnam	10	[470,471]

Arsenic occurrence in the environment, its toxicity, health hazards, and the techniques used for speciation analysis are well known and have been reviewed [5,13–16,555,563,568]. Long-term drinking water exposure causes skin, lung, bladder, and

kidney cancer as well as pigmentation changes, skin thickening (hyperkeratosis) neurological disorders, muscular weakness, loss of appetite, and nausea [14,17,18,1]. This differs from acute poisoning, which typically causes vomiting, oesophageal and abdominal pain, and bloody “rice water” diarrhea [14,17–21].

Arsenic in natural waters is a worldwide problem. Arsenic pollution has been reported recently in the USA, China, Chile, Bangladesh, Taiwan, Mexico, Argentina, Poland, Canada, Hungary, New Zealand, Japan and India [22–28,539,542–544,546,549,551,554,562,573,574] (Table 1). The largest population at risk among the 21 countries with known groundwater arsenic contamination is in Bangladesh, followed by West Bengal in India [29,14,30–32].

The WHO provisional guideline of 10 ppb (0.01 mg/L) has been adopted as the drinking water standard. However, many countries have retained the earlier WHO guideline of 50 ppb (0.05 mg/L) as their standard or as an interim target including Bangladesh and China. In 2001, US-EPA published a new 10 ppb (0.01 mg/L) standard for arsenic in drinking water, requiring public water supplies to reduce arsenic from 50 ppb (0.05 mg/L) [33], which will be effective from January 2006. The maximum

Table 2
Comparison of main arsenic removal technologies

Major oxidation/precipitation technologies	Advantages	Disadvantages
Oxidation/precipitation: [472–478]		
Air oxidation	Relatively simple, low-cost but slow process; <i>in situ</i> arsenic removal; also oxidizes other inorganic and organic constituents in water	Mainly removes arsenic(V) and accelerate the oxidation process
Chemical oxidation	Oxidizes other impurities and kills microbes; relatively simple and rapid process; minimum residual mass	Efficient control of the pH and oxidation step is needed
Major coagulation/coprecipitation technologies		
Coagulation/electrocoagulation/coprecipitation: [405,442,479–499]		
Alum coagulation	Durable powder chemicals are available; relatively low capital cost and simple in operation; effective over a wider range of pH	Produces toxic sludges; low removal of arsenic; pre-oxidation may be required
Iron coagulation	Common chemicals are available; more efficient than alum coagulation on weigh basis	Medium removal of As(III); sedimentation and filtration needed
Lime softening	Chemicals are available commercially	Readjustment of pH is required
Major sorption and ion-exchange technologies		
Sorption and ion-exchange techniques (references for adsorption are given in text): [500–503,547,548,553,557,564–567,569–572]		
Activated alumina	Relatively well known and commercially available	Needs replacement after four to five regeneration
Iron coated sand	Cheap; no regeneration is required; remove both As(III) and As(V)	Not standardized; produces toxic solid waste
Ion-exchange resin	Well-defined medium and capacity; pH independent; exclusive ion specific resin to remove arsenic	High cost medium; high-tech operation and maintenance; regeneration creates a sludge disposal problem; As(III) is difficult to remove; life of resins
Major membrane technologies		
Membrane techniques: [492,504–512,575]		
Nanofiltration	Well-defined and high-removal efficiency	Very high-capital and running cost, pre-conditioning; high water rejection
Reverse osmosis	No toxic solid waste is produced	High tech operation and maintenance
Electrodialysis	Capable of removal of other contaminants	Toxic wastewater produced
Other techniques		
Foam flotation: [513–523,558]		
Solvent extraction: [524]		
Bioremediation: [525,475]		

permissible limits for drinking water in different countries are given in Table 1.

Arsenic removal technologies were reviewed ([9,26,27,34–53,576]). The major arsenic removal technologies are compared in Table 2.

Most remediation methods discussed more effectively remove arsenic from water containing high initial arsenic concentrations (usually >100 mg/L) but residual arsenic concentrations exceed the 0.05 mg/L water quality standard used in most countries. Conventional and non-conventional treatment technologies for aqueous arsenic remediation were compared [54]. In villages in India and Bangladesh, a highly successful technology may not succeed in rural areas unless it fits into the rural circumstances and is well accepted by the masses. Technology development is only possible when a partnership exists involving proper village level participation. Arsenic removal technologies all suffer from one or more drawbacks, limitations and scope of application.

2. Arsenic remediation by adsorption

Adsorption is evolving as a front line of defense. Selective adsorption utilizing biological materials, mineral oxides, activated carbons, or polymer resins, has generated increasing excitement [538,545]. The use of carbon extends far back into history. Its origin is impossible to document. Charcoal was used for drinking water filtration by ancient Hindus in India, and carbonized wood was a medical adsorbent and purifying agent in Egypt by 1500 B.C. [55].

Modern activated carbon industrial production was established in 1900–1901 to replace bone-char in sugar refining [56]. Powdered activated carbon was first produced commercially from wood in Europe in the early 19th century and was widely used in the sugar industry. Activated carbon was first reported for water treatment in the United States in 1930 [57]. Activated carbon is a crude form of graphite with a random or amorphous highly porous structure with a broad range of pore sizes, from visible cracks and crevices, to crevices of molecular dimensions [58]. Active carbons have been prepared from coconut shells, wood char, lignin, petroleum coke, bone-char, peat, sawdust, carbon black, rice hulls, sugar, peach pits, fish, fertilizer waste, waste rubber tire, etc. (Table 3). Wood (130,000 tonnes/year), coal (100,000 tonnes/year), lignite (50,000 tonnes/year), coconut shell (35,000 tonnes/year), and peat (35,000 tonnes/year) are most commonly used [59].

Carbon surface chemistry has been reviewed [56,60,61]. This surface chemistry depends upon the activation conditions and temperatures employed. Activation refines the pore structure. Mesopores and micropores are formed yielding surface areas up to 2000 m²/g [62,61]. Acidic and basic activation carbon exists according to the Steenberg's classification [63]. The acidic groups on activated carbons adsorb metal ions [64]. Surface area may not be a primary factor for adsorption on activated carbon. High surface area does not necessarily mean high adsorption capacity [65].

The adsorption of metal ions on carbon is more complex than uptake of organic compounds because ionic charges affect

Table 3
Alternative feedstocks proposed for the preparation of activated carbons

Bones	Lampblack
Bagasse	Leather waste
Bark	Municipal waste
Beat-sugar sludges	Molasses
Blood	Nut shells
Blue dust	News paper
Coal	Oil shale
Coffee beans	Olive stones
Coconut shell	Petroleum acid sludge
Coconut coir	Pulp-mill waste
Cereals	Palm tree cobs
Carbohydrates	Petroleum coke
Cottonseed hulls	Petroleum acid sludge
Corn Cobs	Potassium ferrocyanide residue
Distillery waste	Rubber waste
Fuller's earth	Rice hulls
Fertilizer waste slurry	Refinery waste
Fish	Reffination earth
Fruit pits	Scrap tires
Graphite	Sunflower seeds
Human hairs	Spent Fuller's earth
Jute stick	Tea leaves
Kelp and seaweed	Wheat straw
Lignin	Wood
Lignite	

removal kinetics from solution. Adsorption capacity depends on activated carbon properties, adsorbate chemical properties, temperature, pH, ionic strength, etc. Many activated carbons are available commercially but few are selective for heavy metals. They are also expensive. Despite carbon's prolific use to treat wastewater, it remains expensive, requiring vast quantities of activated carbon. Improved and tailor-made materials are sought. Substitutes should be easily available, cheap and, above all, be readily regenerated, providing quantitative recovery.

In this review, adsorbents are broadly divided into two classes: (1) commercial and synthetic activated carbons and (2) low-cost adsorbents.

2.1. Commercial and synthetic activated carbons

2.1.1. Commercial activated carbons

Allen and Whitten, 1998 reviewed the production and characterization of activated carbon from many carbonaceous sources. Recently, the science and technology of charcoal production is reviewed [66]. Commercial activated carbons have been extensively used for As(III) and As(V) adsorption from water [67–70]. Activated carbon adsorption was investigated in arsenic and antimony removal from copper electrorefining solutions [67]. A huge arsenic sorption capacity (2860 mg/g) was obtained on this coal-derived commercial carbon. Some activated carbons impregnated with metallic silver and copper were also used for arsenic remediation [71].

Eguez and Cho [68] studied adsorption of As(III) and As(V) on activated charcoal versus pH and temperature. The capacity of As(III) on carbon was constant at pH 0.16–3.5. However As(V) exhibited a maximum adsorption at pH 2.35 over the pH range of 0.86–6.33. The As(III) isosteric heat of adsorp-

tion varied from 4 to 0.75 kcal/mol and that for As(V), from 4 to 2 kcal/mol with increasing surface loading. These magnitudes suggest that physisorption occurred due to weak Van der Waals forces. Activated charcoal adsorbed 2.5 wt.% As(V) and 1.2 wt.% As(III) (based on the weight of carbon) at an equilibrium concentration of 2.2×10^{-2} M of both As(III) and As(V) (Table 5).

Three activated carbons with different ash contents were studied for As adsorption: coconut shell carbon with 3% ash, peat-based extruded carbon with 5% ash and a coal-based carbon with 5–6% ash [69]. More As(V) was removed from water using carbon with a high ash content. Carbon pretreatment with Cu(II) improved arsenic removal capacity. The optimum pH for arsenic adsorption by Cu-pretreated carbon was ~ 6 . Arsenic formed insoluble metal arsenates with the impregnated copper. Arsenic is also simultaneously adsorbed by carbon independently. Arsenic was desorbed using strongly acidic or alkaline solutions.

Arsenic was adsorbed onto activated carbon impregnated with metallic silver and copper [70]. A combination of granular activated carbon and carbon steel wool removed arsenic from water [72]. The adsorption ability of the steel wool was due to iron–arsenic electrochemical reactions.

2.1.2. Synthetic activated carbons

Activated carbons are produced by carbonization employing slow substrate heating in the absence of air below 600 °C. This

removes volatiles. Then chemical or physical activation follows. Treatment with oxidizing agents (steam, carbon dioxide, or oxygen) at elevated temperature or with chemical activants (ZnCl₂, H₂PO₄, H₂SO₄, KOH, K₂S, KCNS, etc.) completes the activation [59,73]. Chemical activants may promote crosslinking forming a rigid, less volatile matrix with a smaller volume contraction going to high temperature. An advantage of chemical activation is the lower temperature required. Chemical activation gives higher global yields since char burn-off is not required. Post activation removes residual catalyst, which may be recovered and reused. Some important feedstocks with activant and other conditions are listed in Table 4 [59].

Several types of activated carbons were synthesized and used for the removal of arsenic from water/wastewater ([74–86,577]).

Gu et al. [75] developed iron-containing granular activated carbon adsorbents (As-GAC) for arsenic removal from drinking water. Granular activated carbon (GAC) was a support for ferric ions that were impregnated using aqueous ferrous chloride (FeCl₂) followed by NaClO chemical oxidation. Carbons produced by lignite steam activation were most suitable among 13 tested activated carbons for iron impregnation and arsenic removal. Maximum iron loadings were 7.89 wt.% for Draco 20 × 50 and 7.65 wt.% for Draco 20 × 40. The BET specific surface area, pore volume, and porosity all decreased after iron impregnation. This indicated some micropores micropore blockage. SEM/X-EDS studies showed iron ($\sim 1\%$ Fe) distributed on the As-6AC carbon surfaces. Iron extended into the gran-

Table 4

Some chemical activant-feedstock couples to prepare activated carbon (extended form of the table provided by Pollard et al. [59])

Feedstock	Activant	Conditions	References
Almond shell, olive stones and peach stones	–	Heating in CO ₂ at 606 °C	[578]
Coconut shell	Con. H ₂ SO ₄	Parts by weight H ₂ SO ₄ for 24 h at 150 °C	[84]
Fertilizer slurry	H ₂ O ₂ /H ₂ O, N ₂	450 °C, 1 h	[579]
Palm tree cobs	H ₃ PO ₄ /H ₂ SO ₄	730 °C, 6 h	[580]
Coconut shell	H ₃ PO ₄	450 °C	[581]
Petroleum coke	KOH/H ₂ O	700–850 °C, 4 h	[56]
Raffination earth	H ₂ SO ₄	10% (v/v), 350 °C	[582]
Algerian coal	KOH/NaOH	930 °C	[583]
Pine saw dust	Fe(NO ₃) ₃ /CO ₂	850 °C, 1 h; 825 °C, 6 h	[584]
Almond and pecan shells	H ₃ PO ₄	Chemical activation with H ₃ PO ₄ /physical CO ₂	[585]
Eucalytus woodchars	–	CO ₂ activation, 400–800 °C	[586]
Bituminous coal	ZnCl ₂	N ₂ /400–700 °C	[587]
Coal or coconut shell	–	Phosgene or chlorine gas at 180 °C	[588]
Petroleum coke	KOH	Dehydration at 400 °C followed by activation in 500–900 °C	[589]
Lignite	Na ₂ MoO ₄ /NaWO ₄ /NH ₄ VO ₃ / (NH ₄) ₂ MoO ₄ /FeCl ₃ /Fe(NO ₃) ₃	Inert atmosphere/600–800 °C	[590]
Peanut hulls	H ₂ SO ₄	150 °C, sodium bicarbonate	Reriasamy and Namasivayam (1995)
Fly ash	–	Froth flotation, hydrophobic char was separated from hydrophilic ash with the help of methyl isobutyl ketone	[76]
Oat hulls	Steam	Fast pyrolysis at 500 °C with inert nitrogen	[77]
Solvent-extracted olive pulp and olive stones	K ₂ CO ₃	Under vacuum and atmospheric pressure; 60 °C/min; 800 °C; activation under N ₂ at 10 °C/min	[95]
Coconut shells and coconut shell fibers	–	Carbonized with H ₂ SO ₄ and activated at 600 °C for 1 h	[526,527,528,560]

Table 5
Comparative evaluation of activated carbons and various low-cost adsorbents for arsenic removal

Adsorbent	Type of water	pH	Concentration/ range	Surface area (m ² g ⁻¹)	Temperature (°C)	Model used to calculate adsorption capacity	Capacity (mg/g)		References
							As(III)	As(V)	
Iron oxide coated sand IOCS	Tap	–	100 µg/L	–	22 ± 2	Langmuir	0.136	–	[151]
Iron oxide coated sand	Drinking	7.6	100 µg/L	10.6	22 ± 2	Langmuir	0.041	0.043	[231]
Iron oxide coated sand, IOCS-2	Tap	7.6	100 µg/L	–	22 ± 2	Freundlich	–	0.008	[148]
Iron oxide coated sand (IOCS)	Natural (dose 0.5–1.20 g/100 mL); 5 h	–	325 µg/L	5.1	–	Langmuir	–	0.018	[152]
Ferrihydrite (FH)	Natural (dose 0.02–0.09 g/100 mL); 5 h	–	325 µg/L	141	–	Langmuir	–	0.25	–
Iron oxide uncoated sand	Drinking (dose 20 g/L); 2 h	7.5	100–800 µg/L	–	27 ± 2	Langmuir	0.006	–	[129,130]
Iron oxide coated sand Al ₂ O ₃ /Fe(OH) ₃	Drinking (dose 20 g/L); 2 h	7.5	100–800 µg/L	–	27 ± 2	Langmuir	0.028	–	–
	Drinking (63.3 g in 50 ML; 100 g in 80 ML)	8.2–8.9	0.05 mg/L	–	–	Breakthrough capacity	–	0.09	[591]
La(III) impregnated silica gel	–	–	–	–	–	–	–	8.85	[529]
Y(III) impregnated alumina	–	–	–	–	–	–	–	14.45	[530]
Pure alumina	–	–	–	–	–	–	–	13.64	–
La(III) impregnated alumina	–	–	–	–	–	–	–	12.88	–
Basic yttrium carbonate	Drinking	9.8–10.5 for As(III) and 7.5–9.0 for As(V)	5.0–0.20 mmol/L for As(III) and 10–60 mmol/L for As(V)	28.6	20, 30, 40	Langmuir	305.8, 356.8, 428.1	352.6, 428.1, 483.4	[313]
Activated alumina	–	–	–	–	–	–	–	11–24	[10]
Waste Fe(III)/Cr(III)	Aqueous solution (dose 500 mg/50 ML; 5 h)	4.0	20–100 mg/L	–	32	Langmuir	–	11.02	[127]
Activated carbon (Draco)	–	–	–	–	–	–	–	3.75	[82]
Char carbon	Aqueous solution	2–3	157–737 for As(V) and 193–992 for As(III)	36.48	25	–	89.0	34.46	[76]
Activated carbon	Aqueous solution	6.4–7.5	157–737 for As(V) and 193–992 for As(III)	43.40	25	–	29.9	30.48	–
Activated Bauxsol (AB)	Water (dose: 5 g/L)	4.5	7.03–220.9 Mm for As(V); 2.04–156.7 Mm for As(III)	130	23 ± 1	Langmuir	0.541	7.642	[115,116]
Bauxsol	Water (dose: 5 g/L)	4.5	0.80–32.00 Mm	–	23 ± 1	Langmuir	–	1.081	–
Bauxsol-coated sand (BCS)	De-ionized/Tap	4.5	0.54–20.34 mg/L	7.56	Ambient	Langmuir	–	3.32	[117]

AB-coated sand (ABCS)	De-ionized/Tap	7.1	0.54–20.34 mg/L	47.29	Ambient	Langmuir	–	1.64	
Seawater-neutralized red mud (Bauxsol)	De-ionized/Tap (dose: 5 g/L)	7.3	0.80–32.00 Mm	–	30	Langmuir	–	1.081	[592]
Red mud (RRM)	Water (dose: 20 g/L)	7.25 for As(III); 3.50 for As(V)	33.37–400.4 $\mu\text{mol/L}$	–	25	Langmuir	0.663	0.514	[112]
Red mud (ARM)	Aqueous solution (dose: 20 g/L)	7.25 for As(III); 3.50 for As(V)	33.37–400.4 $\mu\text{mol/L}$	–	25	Langmuir	0.884	0.941	
Bead cellulose loaded with iron oxyhydroxide (BCF)	Ground water	7.0	1–100 mmol/L	–	25 \pm 0.5	Langmuir	99.6	33.2	[338]
Activated alumina	Drinking water	7.6	1 mg/L	370	25	Langmuir	0.180	–	[198]
Activated alumina (AA)	Drinking water	7.6	–	365	25	Langmuir	–	–	[209]
Iron oxide-impregnated activated alumina (IOIAA)	Drinking water	12	–	200	25	Langmuir	–	–	
MnO ₂ (MO1)	Drinking water	7.9	<1 mg/L	17	25	Langmuir	–	0.172	[195]
Monoclinic hydrous zirconium oxide (Zr resin)	Drinking water	9–10 for As(III); 4–6 for As(V)	1 \times 10 ⁻³ M	373	25	Langmuir	112.4	89.90	[315]
Zr resin	Drinking water	8.0 for As(III); 4.5 for As(V)	0–5 mmol/L	–	25	Langmuir	79.42	53.94	[314]
Iron(III)-loaded chelating resin	Aqueous solution	9.0 for As(III); 3.5 for As(V)	–	–	25	Langmuir	62.93	55.44	[305]
TiO ₂	Drinking water	7.00	–	330	25	Langmuir	59.93	37.46	[217]
TiO ₂ (Hombikat UV 1000)	Drinking water	4.0	<0.0015 M	334	22	Langmuir	22.70	22.47	[220]
TiO ₂ (Degussa P25)	Drinking water	4.0	<0.0015 M	55	22	Langmuir	3.45	4.65	
HFO	Drinking water	9.0	0–60 mg/L	200	22	–	28.0	7.0	[251]
Goethite	Drinking water	9.0	0–60 mg/L	39	22	–	22.0	4.0	
Fe _x (OH) _y -Montm	Drinking water	9.0	0–60 mg/L	165	22	–	13.0	4.0	
Ti ₁ H _y -Montm	Drinking water	9.0	0–60 mg/L	229	22	–	13.0	3.0	
FePO ₄ (amorphous)	Drinking water	7–9 for As(III); 6–6.7 for As(V)	0.5–100 mg/L	53.6	20	–	21	10	[276]
FePO ₄ (crystalline)	Drinking water	7–9 for As(III); 6–6.7 for As(V)	0.5–100 mg/L	35.9	20	–	16	9	
MnO ₂ -loaded resin	Drinking water	7–8.5	3–150 mg/L	–	22	–	53	22	[531,532]
Iron(III) oxide-loaded melted slag (IOLMS)	Wastewaters	2.5	20–300 mg/L	196	20	–	2.9–30.1	18.8–78.5	[123]
TiO ₂	Ground water	7.0	0.4–80 mg/L	251	25	Langmuir	32.4	41.0	[222,291,292]
Activated carbon (AC) produced from oat hulls	Drinking water	5.0	25–200 $\mu\text{g/L}$	522	24	Langmuir	–	3.08	[77]
Zirconium(IV)-loaded chelating resin (Zr-LDA)	Spring water	9.0 for As(III) and 4.0 for As(V)	–	7.3	25	Langmuir	49.15	88.73	[317]

Table 5 (Continued)

Adsorbent	Type of water	pH	Concentration/ range	Surface area (m ² g ⁻¹)	Temperature (°C)	Model used to calculate adsorption capacity	Capacity (mg/g)		References
							As(III)	As(V)	
Methylated biomass	Surface and ground water	6.5	0.5–2.5 Mm	6.5	30	–	–	3.75	[354]
Granular ferric hydroxide (GFH)	Surface and ground water	7.0	–	226–252	24	Freundlich	–	0.004	[234]
Zirconium(IV)-loaded phosphoric chelate adsorbent	NA	2.0	5 Mm	–	25	Column capacity	–	149.9	[319]
Oxisol	Wastewater (soil liner to be used in tailings dams at a sulfidic gold ore plant)	5.5	10–1000 mg/L	35.7	25	Langmuir	2.60	3.20	[269]
Gibbsite	Wastewater (soil liner to be used in tailings dams at a sulfidic gold ore plant)	5.5	10–1000 mg/L	13.5	25	Langmuir	3.30	4.60	
Goethite	Wastewater (soil liner to be used in tailings dams at a sulfidic gold ore plant)	5.5	10–1000 mg/L	12.7	25	Langmuir	7.50	12.5	
Kaolinite	Wastewater (soil liner to be used in tailings dams at a sulfidic gold ore plant)	5.5	10–1000 mg/L	8.5	25	Langmuir	–	<0.23	
Untreated GAC	Drinking water	4.7	0.10–30.0 mg/L	600–1000	25	Langmuir	–	0.038	[75]
GAC-Fe (0.05 M)	Drinking water	4.7	0.10–30.0 mg/L	600–1000	25	Langmuir	–	2.96	
GAC-Fe–O ₂ (0.05 M)	Drinking water	4.7	0.10–30.0 mg/L	600–1000	25	Langmuir	–	1.92	
GAC-Fe–H ₂ O ₂ (0.05 M)	Drinking water	4.7	0.10–30.0 mg/L	600–1000	25	Langmuir	–	3.94	
GAC-Fe–NaClO (0.05 M)	Drinking water	4.7	0.10–30.0 mg/L	600–1000	25	Langmuir	–	6.57	
Zirconium-loaded activated carbon (Zr-AC)	Drinking water	8–9	5–100 mg/L	–	25	Column capacity	–	2.8	[79]
Absorptionsmittel (AM3)	Drinking water	8–9	5–100 mg/L	–	25	Column capacity	–	2	
Granular ferric hydroxide (GIH)	Drinking water	8–9	5–100 mg/L	–	25	Column capacity	–	2.3	
Granular ferric hydroxide (GIH)							–	8.5	[233]
Ferrihydrite			0.267–26.7 mmol/L				266.5	111.02	[235]
Activated alumina grains	Drinking water	7.00 for As(III) and 5.2 for As(V)	0.79–4.90 mg/L for As(III) and 2.85–11.5 mg/L for As(V)	116–118	25	Langmuir	3.48	15.9	[203]
Activated carbon	Wastewater (copper electrorefineries)	–	300 mg/L	1000	25	–	–	2860	[67]
Activated carbon	–	–	–	–	–	–	–	25	[68]
Coconut husk carbon	Industrial wastewater	12.0	50–600 mg/L	206	30	Langmuir	146.30		[84]
Coconut shell carbon with 3% ash	Wastewater (processing of complex sulfide ore)	5.0	0–200 mg/L	1150–1250	25	Langmuir	–	2.4	[69]

Peat-based extruded carbon with 5% ash		5.0	0–200 mg/L	975	25	Langmuir	–	4.9	
Coal-based carbon with 5–6% ash		5.0	0–200 mg/L	1050–1200	25	Langmuir	–	4.09	
Orange juice residue	Wastewater	7–11 for As(III) and 2–6 for As(V)	–	–	30	Langmuir	70.43	67.43	[339]
Phosphorylated crosslinked orange juice residue (POJR1)	Wastewater	2–6	–	–	30	Langmuir	–	39.71	[341]
Phosphorylated crosslinked orange juice residue (POJR2)	Wastewater	2–6	–	–	30	Langmuir	–	70.43	
Phosphorylated crosslinked orange waste (POW)	Wastewater	10 for As(III) and 3 for As(VI)	–	1.75	30	Langmuir	68.18	68.18	[340]
Alumina	Drinking water	6.5	0.133–1.33 mmol/L	768	25	Langmuir	–	8.99	[299]
Al ₁₀ SBA-15	Drinking water	6.5	0.133–1.33 mmol/L	343	25	Langmuir	–	20.98	
Fe ₁₀ SBA-15	Drinking water	6.5	0.133–1.33 mmol/L	–	25	Langmuir	–	12.74	
Ferrihydrite	–	7.0	0–150 mg/L	–	–	Langmuir	–	68.75	[237]
Goethite	–	7.0	0–38 mg/L	–	–	Langmuir	–	442.8	
Biomass	–	2.0	1–10 mg/L	–	28	Langmuir	13.17	–	[355]
Nanoscale zero-valent iron (NZVI)	Ground water	7.0	–	37.2	35	Langmuir	2.47	–	[294]
Cu-EDA-Si (calcined mesoporous silica)	Ground water	–	1–100 mg/L	–	–	–	–	140.0	[298]
Fe/NN-MCM-41	Drinking	6.0	~0–1500 mg/L	310	25	–	–	119.8	[301]
Co/NN-MCM-41	Drinking	6.0	~0–1500 mg/L	580	25	–	–	51.70	
Ni/NN-MCM-41	Drinking	6.0	~0–1500 mg/L	284	25	–	–	38.96	
Cu/NN-MCM-41	Drinking	6.0	~0–1500 mg/L	588	25	–	–	23.97	
Fe/NN-MCM-48	Drinking	6.0	~0–1500 mg/L	352	25	–	–	187.3	
Co/NN-MCM-48	Drinking	6.0	~0–1500 mg/L	634	25	–	–	74.92	
Ni/NN-MCM-48	Drinking	6.0	~0–1500 mg/L	305	25	–	–	64.43	
Cu/NN-MCM-48	Drinking	6.0	~0–1500 mg/L	635	25	–	–	37.46	
Alginate bead (doped and coated with iron)	Drinking	7.0	50 µg/L	–	25	Column capacity	–	0.014	[310]
Uncalcined LDHs	Wastewater (power-plant effluent streams)	4.2–5.4	20–200 mg/L	47	25	Langmuir	–	4.55	[273]
Calcined LDHs	Wastewater (power-plant effluent streams)	4.2–5.4	20–200 mg/L	198	25	Langmuir	–	5.61	
Chitosan	Wastewater	4.0	400 mg/L	–	25	–	–	58	[333]
Dry water hyacinth plant leaf							–	0.34	[359]
Akaganeite β-FeO(OH) nanocrystals	Water/wastewater	7.5	5–20 mg/L	330	25	Langmuir	–	141.3	[242]
Mixed rare earth oxide	Water/wastewater	6.5	50 mg/L	6.75	29	Langmuir	–	2.95	[261]
Fresh biomass	Ground water	6.0	50–2500 mg/L	–	30	Langmuir	128.1	–	[345]

Table 5 (Continued)

Adsorbent	Type of water	pH	Concentration/ range	Surface area (m ² g ⁻¹)	Temperature (°C)	Model used to calculate adsorption capacity	Capacity (mg/g)		References
							As(III)	As(V)	
Immobilized biomass	Ground water	6.0	50–2500 mg/L	–	30	Langmuir	704.1	–	
Manganese ore	Ground water	6.3 for As(III) and 6.5 for As(V)	–	–	–	Langmuir	0.53	15.38	[135]
Polymetallic sea nodule	Ground water/tubewell water	6.0 for As(III); 2.0 for As(V)	0–0.7 mg/L for As(III); 0–1.0 mg/L for As(V)	–	–	Langmuir	0.69	2.85	[270]
Portland cement	Drinking water	4–5	0.2 mg/L	15.38	30	Langmuir	–	3.98	[262]
Iron oxide coated cement (IOCC)	Drinking water	~7	0.5–10.0 mg/L	–	35	Langmuir	–	6.43	[263]
Iron oxide coated cement (IOCC)	Drinking water	~7	0.7–13.5 mg/L	–	35	Langmuir	0.67	–	[264]
ZMA (Sonora)	Ground water	4.0	0.1–4 mg/L	279	22	Langmuir	0.0048	0.1	[180,181]
ZME (Oaxaca)	Ground water	4.0	0.1–4 mg/L	51	22	Langmuir	0.0028	0.025	
ZMS (San Luis Potosi)	Groundwater	4.0	0.1–4 mg/L	22	22	Langmuir	0.017	0.1	
ZMT (Puebla)	Ground water	4.0	0.1–4 mg/L	28	22	Langmuir	0.003	0.05	
ZH	Groundwater	4.0	0.1–4 mg/L	–	22	Langmuir	0.002	0.006	
Shirasu-zeolite (SZP ₁)	Drinking water	3–10	1.3 Mm	15.6	24	Freundlich	–	65.93	[182]
Aluminum-loaded Shirasu-zeolite (Al-SZP ₁)	Drinking water	3–10	1.3 Mm	–	24	Freundlich	–	10.49	
Sulfate-modified iron oxide-coated sand (SMIOCS)	Drinking water	4–10	0.5–3.5 mg/L	3.74	27	Langmuir	–	0.13 (pH 4), 0.12 (pH 7), 0.08 (pH 10)	[154]
Modified iron oxide-coated sand (SMIOCS)	Drinking water	7.2	0.5–3.5 mg/L	2.9–7.9	50	Langmuir	0.14	–	[153]
Tea fungal biomass	Ground water	7.20	1.3 for As(III) and 0.9 mg/L for As(V)	–	30	Freundlich	1.11	4.95	[349]
FeCl ₃ treated tea fungal biomass	Ground water	7.20	1.3 for As(III) and 0.9 mg/L for As(V)	–	30	Freundlich	5.4	10.26	
<i>Penicillium purpurogenum</i>	–	5.0	10–750 mg/L	–	20	Langmuir	35.6	–	[348]
Human hairs	Drinking water	–	90–360 µg/L	–	22	Langmuir	–	0.012	[372]
Nanostructured akaganeite	–	7.5	5–20 mg/L	330	25	Langmuir	–	1.80	[240]
Activated carbon	–	–	–	–	–	–	–	20	[593]
Chitosan/chitin mixture	–	–	–	–	–	–	–	0.13 µequiv. As/g	[334]
Chrome sludge waste	–	–	–	–	–	–	–	21	[360]
Hematite	Water/wastewater	4.2	133.49 µmol/L	14.40	30	Langmuir	–	0.20	[134]
Feldspar	Water/wastewater	4.2	133.49 µmol/L	10.25	30	Langmuir	–	0.18	

Aluminum-loaded coral limestones (Al-CL)	Drinking water	2–11	2.0–5.0 mg/L	–	24–25	Freundlich	–	0.15	[160]
Amine-modified coconut coir							–	6.44	[302]
Fe(III) alginate gel	–	4.0	0–10 mg/L	–	–	–	–	352	[307]
Poly(ethylene mercaptoacetimide) (PEM)	–	8.0 for As(III) and 2.0 for As(V)	–	–	24	Langmuir	31.56	112.7	[322]
Olivier soil	Soil	5–6	5–100 mg/L	–	25	Langmuir	–	0.42	[139]
Sharkey soil	Soil	5–6	5–100 mg/L	–	25	Langmuir	–	0.74	
Windsor soil	Soil	5–6	5–100 mg/L	–	25	Langmuir	–	0.55	
Mycon (<i>P. chrysogenum</i>)	Wastewater	3.0	1–300 mg/L	–	25	Langmuir	–	24.52	[353]
Mycon/HDTMA	Wastewater	3.0	1–300 mg/L	–	25	Langmuir	–	57.85	
Mycon/magnafloc	Wastewater	3.0	1–300 mg/L	–	25	Langmuir	–	56.08	
Mycon/DA	Wastewater	3.0	1–300 mg/L	–	25	Langmuir	–	33.31	
Cu(II)-Dow2N resin							–	44.00	[304]
Zr(IV)-loaded phosphoric acid chelating resin (RGP)	River/sea water	1.14	2.5 mmol/L	29.2	–	Column capacity	–	49.0	[320]
Molebdate-impregnated chitosan gel beads (MCCB)							–	200	[335]
Iron hydroxide coated alumina	Drinking water	6.62–6.74 for As(III) 7.15–7.2 for As(V)	0.1–1.8 mmol/L	95.7	25	Langmuir	7.64	36.64	[215]
Ferric chloride impregnated silica gel	–	–	–	–	–	–	≤5.24	≤5.24	[277]
Titanium dioxide-loaded Amberlite XAD-7 resin	Drinking water/wastewater	1–5 for As(V) and 5–10 for As(III)	0–5 mmol/L	209	25	Langmuir	9.74	4.72	[323]
Iron(III)-loaded chelating resin							–	60.0	[311]
Water lettuce (<i>Pistia stratiotes</i> L.).	–	–	–	–	–	–	–	1.43	[346]
<i>Penicillium purpurogenum</i>	–	5.0	10–750 mg/L	–	20	Langmuir	35.6	–	[347]
GAC	Drinking/wastewater	7.0	1 mg/L	1.065	20–23	–	0.09	4.5	[86]
Fe(III) oxide-impregnated GAC	Drinking/wastewater	7.0	1 mg/L	840	20–23	–	4.50	4.5	
Iron(III) oxide with polyacrylamide	–	–	–	–	–	–	–	43.0	[533]
Humic acid	–	–	–	–	–	–	–	7.9	[534]
Activated alumina	Drinking water/ground water	7.0	50 mg/m ³	195	25	Langmuir	–	9.20	[535]

Table 5 (Continued)

Adsorbent	Type of water	pH	Concentration/ range	Surface area (m ² g ⁻¹)	Temperature (°C)	Model used to calculate adsorption capacity	Capacity (mg/g)		References
							As(III)	As(V)	
Activated carbons from olive pulp and olive stone, carbon A	Drinking water	7.0	5–20 mg/L	1030	25	Langmuir	1.393	–	[95]
Activated carbons from olive pulp and olive stone, carbon B	Drinking water	7.0	5–20 mg/L	1850	25	Langmuir	0.855	–	
Activated carbons from olive pulp, olive stone, carbon C	Drinking water	7.0	5–20 mg/L	1610	25	Langmuir	0.738	–	
Activated carbons from olive pulp, olive stone, carbon D	Drinking water	7.0	5–20 mg/L	732	25	Langmuir	0.210	–	
Synthetic hydrotalcite <i>L. nigrescens</i>	Ground water	7.0	400 mg/L	–	25	Langmuir	–	105	[275]
	Copper smelting wastewaters	2.5	50–600 mg/L	–	25	Langmuir	–	45.2	[405,350]
Goethite	–	5.0	5–25	103	29	Langmuir	–	~5	[170]
cFeMn	Drinking water	3.0	100 µg/L to 100 mg/L	–	25	–	14.7	8.5	[594]
Drinking water treatment residuals (WTRs)	Drinking water	6.0–6.5	375–3000 mg/L	–	23	Freundlich	~15	~15	[133]
Pisolite	River water	6.5	50 mg/L	61.4	25	–	–	1.29	[136]
Activated pisolite	River water	6.5	50 mg/L	90.45	25	–	–	3.17	
Modified calcined bauxite	Ground water	~7.0	0.5–8.0 mg/L	–	25	Langmuir	–	1.57	[119]
Modified calcined bauxite	Ground water	6–8	0.5–8.0 mg/L	–	25	Freundlich	1.37	–	[122]
Coconut coir pith anion exchanger (CP-AE)	Ground water/industrial effluents	7.0	5.0–100 mg/L	175	20	Langmuir	–	13.57	[324]
		7.0	5.0–100 mg/L	175	30	Langmuir	–	12.51	
		7.0	5.0–100 mg/L	175	40	Langmuir	–	11.67	
		7.0	5.0–100 mg/L	175	50	Langmuir	–	10.42	
Hybrid (poly- mer/inorganic) fibrous sorbent (FIBAN-As)	Drinking water	7.7	–	–	20	Langmuir	75.67	81.66	[254]
Pine wood char	Drinking water	3.5	10–100 µg/L	2.73	25	Langmuir	0.0012	–	[103]
Oak wood char	Drinking water	3.5	10–100 µg/L	2.04	25	Langmuir	0.006	–	
Oak bark char	Drinking water	3.5	10–100 µg/L	25.4	25	Langmuir	0.0074	–	
Pine bark char	Drinking water	3.5	10–100 µg/L	1.88	25	Langmuir	12	–	

ule centers at high iron loads (~6% Fe). When iron content was >~7%, an iron ring formed at the edges of the GAC particles. X-ray diffraction patterns were the same for untreated and 4.12% iron-GAC, suggesting that impregnated iron was amorphous. Arsenic was most efficiently when the iron content was ~6%. Further increases in iron decreased arsenic adsorption. The removal of arsenate occurred in a wide pH range (4.4–11), but arsenate adsorption decreased at pH > 9.0. Phosphates and silicate significantly decreased arsenate removal at pH > 8.5, while sulfate, chloride, and fluoride had minimal effects. The maximum adsorption capacities of untreated GAC, GAC-Fe (0.05 M), GAC-Fe-O₂ (0.05 M), GAC-Fe-H₂O₂ (0.05 M), GAC-Fe-NaClO (0.05 M) were 3.78×10^1 , 2.96×10^3 , 1.92×10^3 , 3.94×10^3 , 6.57×10^3 $\mu\text{g As/g}$, respectively (Table 5). As(V) and As(III) were removed to below 10 $\mu\text{g/L}$ within 6000 empty bed volumes when the groundwater containing approximately 50 $\mu\text{g/L}$ of arsenic was treated.

As(V) and As(III) removal from water was studied using a char carbon (CC) derived from fly ash. Darco activated carbon [Darco S-51 (DC)] obtained from Norit Americas Inc and carbon produced by a graphite electric arc (AC). CC and AC adsorbents removed almost equal amounts of As(V) at optimum conditions; however, percent As(III) removal was more on CC than AC. DC sample was ineffective for both As(III) and As(V) removal. The maximum uptakes of As(V) were 34.5 mg/g (490 ppm, pH 2.2) for CC versus 30.5 mg/g (159 ppm, pH 7.5) for AC. Those of As(III) were 89.2 (709 ppm and pH 2.2) for CC and 29.9 (992 ppm and pH 7.0) mg/g for AC. These sorbents contain different amounts of ash (28.4% for CC and 0.2% for AC). Since their specific surface areas are very similar, the ash contents alone did not greatly influence the adsorption of As(V).

The efficiency of As(V) adsorption by activated carbon (AC) produced from oat hulls [77]. Adsorption capacity decreased from 3.09 to 1.57 mg As g⁻¹ when the initial pH increased from 5 to 8. A modified linear driving force model [87–90] coupled with the Langmuir isotherm described simultaneous rapid and slow kinetic process. The LDF model assumes that the uptake is linearly proportional to a driving force, defined as the difference between the surface concentration and the average adsorbed phase concentration. The simulation results indicate that the adsorption process is described well by the modified LDF model. Because the adsorbate is adsorbs easily on the surface (or macropore surface) of the adsorbent, rapid adsorption results. In the interior (or micropore surface) of the adsorbent, the adsorbate would be adsorbed by a pore and/or surface diffusion mechanism, resulting in a slower adsorption.

As(V) removal by an iron oxide-impregnated activated carbon was modeled by Vaughan and Reed [78] using the surface complexation model (SCM) approach given by Dzombak and Morel [91] and Reed and Matsumoto [92]. As(V) removal was strongly pH dependent. A two-monoprotic site-triple layer model described As(V) removal using two fitting parameters.

Daus et al. [79] studied As(III) and As(V) adsorption onto five different sorbents [activated carbon (AC), zirconium-loaded activated carbon (Zr-AC), a sorption medium with the trade-name 'Absorptionsmittel 3' (AM3), zero-valent iron (Fe⁰), and

granulated iron hydroxide (GIH)]. Batch and column methods were used [80]. The sorption of arsenate followed the sequence Zr-AC \gg GIH = AM3 > Fe⁰ > AC. A different order was found for arsenite (AC \gg Zr-AC = AM3 = GIH = Fe⁰). AC enhanced arsenite oxidation to arsenate in anaerobic batch experiments.

Activated carbon was pretreated with iron-salt solutions to improve arsenic adsorption [81]. The salt type and concentration, pH, and treatment time were examined to improve removal capacity. A 10-fold capacity increase was finally achieved versus the untreated activated carbon. Ferrous ions were adsorbed and As removal was enhanced by arsenate complex formation. Huang and Fu [82] examined the As(V) capacity of 15 brands of activated carbon over a wide pH range. The carbon type, total As(V) concentration and pH were major factors controlling As(V) removal. Treating As(V)-laden activated carbon with a strong acid or base effectively desorbed As(V) but did not restore the As(V) adsorption capacity. Modified sawdust carbon was used to adsorb As(III) [83].

Manju et al. [84] prepared a coconut husk carbon (CHC) by carbonizing one part of coconut husk with 1.8 parts by weight of sulfuric acid (18 M) at 150 °C for 24 h. The carbonized material (CHC) was water washed to remove acid and dried at 105 °C. The CHC (10 g) was mixed with 100 mL of 100 mmol/L copper solution (initial pH 8.5). The mixture was shaken for 24 h at 30 °C and filtered. The filtrate's pH was 6.5. The resulting copper-impregnated coconut husk carbon (CuCHC) was water washed until the filtrate was copper free. Optimum As(III) adsorption conditions on this copper-impregnated activated carbon were established. Maximum adsorption capacity occurred at pH 12.0. Capacity increased going from 30 to 60 °C. Spent adsorbent was regenerated using 30% H₂O₂ in 0.5 M HNO₃.

Peraniemi et al. [93] used zirconium-loaded activated carbon and successfully removed arsenic, selenium, and mercury.

Carbons were also produced from two batches of shale resin (light, medium and heavy) by heating with hexamethylenetetramine [94]. Granulated carbonized adsorbents were prepared from these polycondensates and also from coal dust and a wood resin binder. Arsenic was removed from effluents after steam-activating these adsorbents. Recently arsenic(III) was removed from aqueous solution (concentration range of 5–20 mg/L) by activated carbons developed from olive stones and solvent-extracted olive pulp [95]. The adsorbent was tested at concentrations from 5 to 20 mg/L. Langmuir adsorption capacities for As(III) removal on these carbons were compared to commercially available carbons (Table 5). Mondal et al. [26,27] removed arsenic from a simulated contaminated ground water by adsorption onto Fe³⁺-impregnated granular activated carbon (GAC-Fe) in the presence of Fe²⁺, Fe³⁺, and Mn²⁺. The effects of shaking time, pH, and temperature on the percentage removal of As(Total), As(III), As(V), Fe²⁺, Fe³⁺, and Mn have been reported. The shaking time for optimum arsenic removal was 8 h for GAC-Fe and 12 h for GAC, respectively. Maximum As(V) and As(III) removal was in the pH range of 5–7 and 9–11, respectively, for both the adsorbents.

Iron-containing mesoporous carbon (IMC) was prepared from a silica template (MCM-48) and used for arsenic removal from drinking water [96]. The mesoporous carbon was synthe-

sized by *in situ* polymerization of resorcinol with formaldehyde (RF) in the porous structure of the silica template in a basic aqueous solution, followed by carbonization in an inert atmosphere and template removal. The IMC was obtained by impregnating ferrous chloride into mesoporous carbon followed by sodium hypochloride oxidation. The IMC had a BET surface area of 401 m²/g, slightly lower than that of mesoporous carbon (503 m²/g). Maximum adsorption capacities of 5.96 mg As/g for arsenite and 5.15 mg As/g for arsenate were obtained.

2.2. Low-cost adsorbents

2.2.1. Agricultural products and by-products

Agricultural wastes are by-products, currently unused or underused for animal feed. Agricultural waste/by-products such as rice husks were used for arsenic removal from water. Maximum adsorption occurred at 0.01 mol/L of HNO₃, HCl, H₂SO₄ or HClO₄ using 1.0 g of adsorbent for 5.97 × 10⁻³ mol/L of arsenic for 5 min. The Freundlich isotherm was followed over concentration range from 8.69 × 10⁻⁵ to 1.73 × 10⁻³ mol/L arsenic ($1/n=0.83$ and $K=4.43$ mmol/g). The uptake of arsenic increased with increasing temperature [97].

Untreated rice husk was utilized for aqueous arsenic remediation [595]. Complete removal (using rice husk columns) of both As(III) and As(V) was achieved under the following conditions: initial As concentration, 100 µg/L; rice husk amount, 6 g; average particle size, 780 and 510 µm; flow rate, 6.7 and 1.7 mL/min; and pH, 6.5 and 6.0, respectively. Desorption (71–96%) was also achieved with 1 M of KOH.

2.2.2. Industrial by-products/wastes

2.2.2.1. Chars, and coals. Lignite, peat chars [98–101] bone-char [102] use in wastewater treatment has received increasing attention [98,99], biochar [103,104]. They may be good substitutes for activated carbons. They are plentiful, inexpensive and locally available. Review articles have also appeared [105–109] on the properties, availability, and use of peat in the control of industrial wastewater pollution. Arsenic(V) removal from aqueous solution by mixture of synthetic hydroxylapatite and baryte or bone-char was carried out [102] in the concentration range of 4–100 mg/L. Although the hydroxylapatite and baryte mixture had a small influence on arsenic concentrations, bone-char was found to be a very effective sorbing agent for As(V) in the pH range of 2–5.

Biochar by-products from fast wood/bark pyrolysis, were investigated as adsorbents for the removal of the As³⁺, Cd²⁺, Pb²⁺ from water [103]. Oak bark, pine bark, oak wood, and pine wood chars were obtained from fast pyrolysis at 400 and 450 °C in an auger-fed reactor and characterized. Sorption studies were performed at different temperatures, pHs and solid to liquid ratios in the batch mode. Maximum adsorption occurred over a pH range of 3–4 for arsenic and 4–5 for lead and cadmium. The equilibrium data were modeled with the help of Langmuir and Freundlich equations. Overall, the data were well fitted with both the models, with a slight advantage for Langmuir model. As(III) removal followed the order: pine wood char (1.20 µg/g) < oak wood char (5.85 µg/g) < oak bark char

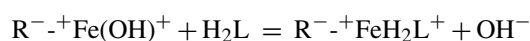
(12.1 µg/g) < pine bark char (12.15 µg/g). This study shows that by-product chars from bio-oil production might be used as plentiful inexpensive adsorbents for water treatment (arsenic remediation) at a value above their pure fuel value. Further studies of such chars, both untreated and after activation, seem warranted as part of the efforts to generate by-product value from biorefineries.

2.2.2.2. Red mud. Red mud is a waste material formed during the production of alumina when bauxite ore is subjected to caustic leaching. A typical Bayer process plant generates a 1–2 tonnes of red mud per ton of alumina produced [110]. Red mud has been explored as an alternate adsorbent for arsenic [111,112]. An alkaline aqueous medium (pH 9.5) favored As(III) removal, whereas the acidic pH range (1.1–3.2) was effective for As(V) removal [111]. The capacities were 4.31 µmol g⁻¹ at the pH of 9.5 for As(III) and 5.07 µmol g⁻¹ at the pH of 3.2 for As(V) (Table 5). Heat and acid treatments on red mud increased its adsorptive capacity [112]. Arsenic adsorption on acid and heat treated red mud is also pH-dependent, with an optimum range of 5.8–7.5 for As(III) and 1.8–3.5 for As(V) [112]. Adsorption followed a first-order rate expression and fit the Langmuir isotherm well. Isotherms were used to obtain the thermodynamic parameters. The As(III) adsorption was exothermic, whereas As(V) adsorption was endothermic [111,112]. As(V) removal by using liquid phase of red mud (LPRM) was also reported [113]. Authors suggested that it is advantageous to use a waste material of red mud liquid phase in the treatment of arsenical wastewater, possibly conjunction with red mud solids as adsorbent.

Seawater-neutralized red muds (Bauxol) [114], Bauxsol activated by acid treatment, and by combined acid and heat treatment, and Bauxsol with added ferric sulfate or aluminum sulfate [115], activated Bauxsol (AB), and chemically modified and activated Bauxsol (AB)-coated sand [116,117] were all applied to arsenic removal. Seawater-neutralized red mud (not activated) was prepared by suspending the red mud in the seawater solution and stirring until equilibrium pH was achieved [114]. Adsorption increased with decreasing pH (i.e., ligand-like adsorption), higher adsorbent dosages, and lower initial arsenate concentrations. Arsenate adsorption decreased in the presence of HCO₃⁻, while Cl⁻ had little effect and Ca²⁺ increased arsenic adsorption. Water quality assessment after treatment with Bauxsol indicated that none of the trace elements tested were released from the adsorbent. A TCLP leaching test also revealed that the adsorbent was not toxic. The sorption capacity of this Bauxsol was 14.43 µmol/g (Table 5). The acid treatment alone, as well as in combination with heat treatment, increased arsenic removal efficiency [115,116]. Combined acid/heat treatment provided best removal [115]. Addition of ferric sulfate or aluminum sulfate suppressed arsenic removal. The activated Bauxsol (AB) produced using combined acid and heat treatment removed roughly 100% of the arsenate (at pH 4.5) with or without the presence of competing anions (i.e., phosphate, bicarbonate, and sulfate) at an initial arsenate concentration of ≤2 mg/L. Combined acid and heat treatments were performed by refluxing Bauxsol in HCl, adding ammonia for complete precipitation, filtering, washing with distilled water (DIW), and calcining at 500 °C for 2 h [116].

The optimal pH for As(V) and As(III) adsorption were 4.5 and 8.5, respectively. The adsorption data fitted the linear form of the Langmuir isotherm. The FITEQL and PHREEQC models were used to predict As(V) adsorption at various pH values (based on diffuse double layer models). The kinetics followed a pseudo-first-order rate expression. Chemically modified Bauxsol and activated Bauxsol (AB)-coated sand were also investigated to remove As(V) from water [117]. Bauxsol-coated sand (BCS) and AB-coated sand (ABCS) were prepared by mixing Bauxsol or AB with wet sand and drying. The adsorption capacities of 3.32 and 1.64 mg/g at pH 4.5 and 7.1, respectively for BCS; and of 2.14 mg/g for ABCS at pH 7.1 were reported (Table 5).

The surface of Bauxsol and activated Bauxsol particles at pH 4.5 primarily covered by positively charged surface groups, which adsorb the negatively charged arsenate anions by electrostatic attraction:



where R is a surface, L is a ligand (arsenate anions, e.g., $H_2AsO_4^{-}$), and $R^{-} \cdot \cdot^{+} Fe(OH)^{+}$ is a surface species. When ferric sulfate or aluminum sulfate is added both coagulation and adsorption take place. Coprecipitation was postulated to take place in the system:



It is clear that ligands (arsenate anions, e.g., $H_2AsO_4^{-}$) are adsorbed on iron hydroxide flocs as Fe complexes. A similar mechanism was given for aluminum sulfate.

Recently Brunori et al. [118] also utilized red mud for treating contaminated waters and soils with particular attention to the Italian regulatory system. Experiments studied the metal trapping ability of treated red mud and the subsequent release of these trapped metals at low pH conditions. The treated red mud exhibited a high metal trapping capacity and metal release at low pH was generally low. The removal capability of treated red mud was increased using more mud in contact with the solution. After 48 h, only 35% of As (corresponding to an absolute value of 230 $\mu\text{g/L}$) was removed with 2 g/L, but the percentage significantly increased up to 70% (corresponding to an absolute value of 400 $\mu\text{g/L}$) with 10 g/L.

Modified calcined bauxite was also used for As(III) and As(V) remediation from ground water [119–122] in batch and column modes. The optimum pH was ~ 7.0 for both As(III) and As(V). Adsorption was unaffected by temperature variations [119]. No appreciable ionic effects except from SO_4^{2-} and EDTA were observed from the background ions including Ca^{2+} , Fe^{3+} , Cl^{-} , NO_3^{-} , PO_4^{3-} and F^{-} . Sorption capacities were calculated using Langmuir model (Table 5).

2.2.2.3. Blast furnace slag. Steel plants generate a large volume of granular blast furnace slag. It is being used as filler or in the production of slag cement. Recently, it was converted into an effective and economical scavenger and utilized for the remediation of aqueous arsenic [123,124].

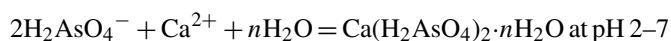
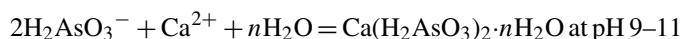
Zhang and Itoh [123] synthesized an adsorbent for aqueous arsenic removal by loading iron(III) oxide onto melted municipal solid waste incinerator slag. The simultaneous generation of

amorphous hydrous ferric oxide sol and a silica sol *in situ* eventually led to the formation of Fe–Si surface complexes which tightly bonded the iron oxide to the slag. For comparison, amorphous hydrous ferric oxide was also prepared. Loading of iron oxide on the slag increased the surface area of iron(III) oxide-loaded melted slag (IOLMS) by 68% compared to FeOOH, which could be attributed to the porous structure formed in IOLMS during the synthesis process. This adsorbent effectively removed both arsenate and arsenite, exhibiting removal capacities for As(V) and As(III) 2.5 and 3 times of those of amorphous hydrous ferric oxide, respectively. About 15 g of IOLMS is sufficient to remove 200 mg As(V) from 1 L of aqueous solution to meet the metal ion concentrations allowed by regulations for industrial wastewater discharge. In contrast 65 g of IOLMS was necessary to remove As(III) from 1 L solution to meet the permissible limit.

Arsenic removal by IOLMS occurred by (1) affinity adsorption, (2) reaction with iron oxides and (3) reaction with calcium and other metallic elements initially contained in the slag. Affinity adsorption dependent on the surface area of IOLMS while chemical reactions depended on the existing forms of the arsenic species. The dominant arsenic species in aqueous solution correlated closely with the solution pH. In the pH range of 2–7, As(V) may be removed through the following reaction since $H_2AsO_4^{-}$ predominates:



On the other hand, calcium and other metallic elements in the slag are also supposed to be effective for As(III) and As(V) removal in terms of the following reactions:



These routes are better for As(V) removal than As(III) since As(III) is generally available as neutral molecules at $\text{pH} < 9$, and trace amounts of metallic elements could be leached out at $\text{pH} > 9$. The removal of As(III) at $\text{pH} \sim 10$ could be explained by the above Ca^{2+} coagulation route, i.e., anionic $H_2AsO_3^{-}$ predominates at $\text{pH} \sim 10$. Thus, $Ca(H_2AsO_3)_2 \cdot nH_2O$ could form from Ca^{2+} in the leachate, and if the solution pH increases only small amounts of Ca^{2+} could be leached, while neutral H_3AsO_3 could not react with Ca^{2+} at $\text{pH} < 9$. Zhang and Itoh [125] also used photocatalytic oxidation of arsenite and removal using slag-iron oxide– TiO_2 adsorbent. The oxidation of arsenite was rapid, but the adsorption of the generated arsenate was slow. A concentration of 100 mg/L arsenite was oxidized to arsenate within 3 h in the presence of adsorbent and under UV-light, but the reaction rate was approximately 1/3rd of the photocatalyzed reaction. The optimum application pH for the adsorbent for oxidation and adsorption was ~ 3.0 .

Elemental iron, iron oxides, Ca–Fe oxides and calcium hydroxides from typical steel manufacturing processes were tested as adsorbents for treating mine-tailing leachate with high As concentrations [124]. These by-products were placed *in situ* as permeable reactive barriers to control arsenic release. Evaporation cooler dust (ECD), oxygen gas sludge (OGS), basic

oxygen furnace slag (BOFS) and, to a lesser degree, electrostatic precipitator dust (EPD) effectively removed both As(V) and As(III). ECD, OGS and BOFS reduced As concentrations to <0.5 from 25 mg/L As(V) or As(III) solution in 72 h. Each exhibited higher As removal capacities than zero-valent iron. High Ca concentrations and alkaline conditions (pH ca. 12) provided by the dissolution of Ca hydroxides may promote the formation of stable, sparingly soluble Ca–As compounds. At an initial pH of 4, As reduction was enhanced by adsorption onto iron oxides. The elution rate of As adsorbed onto OGS and ECD decreased with treatment time. Thus, increasing the residence time within the permeable barrier would enhance As immobilization. ECD was found to be the most efficient barrier material to increase pH and to remove both As and dissolved metals in real tailing leachate. Authors did not attempt to determine the monolayer sorption capacities of various adsorbents. Kanel et al. [126] used blast furnace slag (BFS) for aqueous As(III) remediation. The maximum As(III) adsorption capacity by BFS was 1.40 mg As(III)/g of BFS at 1 mg/L As(III) initial concentration. Oxidation of As(III) to As(V) and its adsorption/precipitation onto BFS was the dominating mechanism.

2.2.2.4. Fe(III)/Cr(III) hydroxide waste. Chromium(VI) compounds are used as corrosion inhibitors in cooling water systems in industries. Fe(II), generated electrolytically, reduces chromium(VI) in the wastewater to Cr(III) under acidic conditions. The Fe(III)/Cr(III) ions produced in solution are precipitated as Fe(III)/Cr(III) hydroxide by the use of lime. The resultant sludge is discarded as waste. Namasivayam and Senthilkumar [127] adsorbed As(V) from water onto a Fe(III)/Cr(III) hydroxide waste generated electrolytically in the treatment of Cr(VI)-containing wastewaters from fertilizer production. As(V) concentration, agitation time, adsorbent dosage, adsorbent particle size, temperature, and pH were studied. The adsorption capacity was evaluated using both Langmuir and Freundlich isotherm models. As(V) adsorption followed a first-order rate expression and was independent of the initial pH (3–10). Adsorption was explained by considering ZPC of the adsorbent material. The pH_{ZPC} of waste Fe(III)/Cr(III) hydroxide was 8.3. In the pH range 3–7, $H_2AsO_4^-$ was predominantly adsorbed. The adsorbent acquired positive charge in this pH range and adsorption was facilitated by Coulombic interactions. In the pH range 7–10, specific interactions occurred, since dissociation of arsenic acid is expected. The transfer of a proton to the hydroxyl groups of the Fe(III)/Cr(III) hydroxide surface is also possible. A surface complexation model has also been proposed for As(V) adsorption on Fe(III)/Cr(VI) waste. Desorption of As(V) from the spent adsorbent was also achieved using NaOH solutions.

Chrome sludge, a waste material from electroplating, was tested to adsorb As(V) from aqueous solutions [128]. The maximum sorption capacity of chrome sludge for As(V) was 21 mg/g (Table 5).

2.2.2.5. Fly ash. Coal combustion produces a huge amount of by-product fly ash, whose disposal requires large quantities of land and water. Currently, its applications are limited to civil

engineering uses including cement and brick production and roadbeds. Bottom ash can also serve as an adsorbent [129,130]. Resource recovery from coal fly ash is one of the most important issues in waste management worldwide. Since the major chemical compounds contained in fly ash are aluminosilicate, intensive efforts have been recently made to utilize this material as an adsorbent.

Fly ash obtained from coal power stations was examined for As(V) removal from water and to restrict As(V) migration in the solid wastes or the soil [131]. Kinetic and equilibrium experiments were performed to evaluate the As(V) removal efficiency by lignite-based fly ash. Removal at pH 4 was significantly higher than that at pH 7 or 10. Maple wood ash without any chemical treatment was also utilized to remediate As(III) and As(V) from contaminated aqueous streams in low concentrations [132]. Static tests removed $\leq 80\%$ arsenic while the arsenic concentration was reduced from 500 to <5 ppb in dynamic column experiments.

2.2.2.6. Miscellaneous. Drinking water treatment residuals (WTRs) were also evaluated for As(V) and As(III) removal [133]. The Al-WTR effectively removed As(V) and As(III) while Fe-WTR removed more As(III) than As(V) in the pH range of 6.0–6.5.

Singh et al. [134] employed hematite and feldspar to As(V) removal from aqueous systems at different pHs, temperatures, and adsorbent particle size. Uptake followed first-order kinetics and fitted the Langmuir isotherm. The maximum removal was 100% with hematite (pH 4.2) and 97% with feldspar (pH 6.2) at an arsenic concentration of 13.35 $\mu\text{mol/L}$. Arsenate adsorption was favored electrostatically up to the pH_{ZPC} (7.1 for hematite and 8.5 for feldspar) of the adsorbents. Beyond this point, specific adsorption played an important role. The decrease in the extent of adsorption below pH 4.2 in case of hematite and below pH 6.2 in case of feldspar attributed to the dissolution of the adsorbents and a consequent decrease in the number of adsorption sites.

A low-cost ferruginous manganese ore (FMO) removed both As(III) and As(V) from groundwater without any pretreatment in the pH range of 2–8 [135]. The major mineral phases present in the FMO were pyrolusite ($\beta\text{-MnO}_2$) and goethite [$\alpha\text{-FeO(OH)}$]. The FeO(OH) can directly adsorb arsenite and arsenate anions. Pyrolusite ($\beta\text{-MnO}_2$), the major mineral phase of the FMO behaved in a manner similar to hydrous manganese oxide, MnO(OH), because of the presence of chemically bound moisture. As(III) adsorbed more strongly than As(V). Once adsorbed, arsenic did not desorb in the pH range of 2–8. Bivalent cations, Ni^{2+} , Co^{2+} , Mg^{2+} , enhanced the adsorption capability of the FMO. The cost of the FMO was $\sim 50\text{--}56$ US\$ per metric ton. This is much cheaper than the commercially available carbons. Recently, pisolite, which is a waste material from Brazilian manganese ore mines, was used for arsenic removal [136]. Both pisolite and activated pisolite were tested in batch and column modes. Maximum loadings of 1.5 and 3.5 mg/g were obtained for Pisolite and activated pisolite at pH 6.5.

Arsenite sorption on galena (PbS) and sphalerite (ZnS) was investigated as a function of solution composition and char-

acterized using X-ray absorption spectroscopy [137]. Arsenite sorbed appreciably only at $\text{pH} > \sim 5$ for PbS and $\text{pH} \sim 4.5$ for ZnS. Arsenite adsorption on PbS and ZnS resulted in the conversion from As-O to As-S coordination. Arsenite does not adsorb through ligand-exchange of surface hydroxyl or sulfhydryl groups. Rather, it forms a polynuclear arsenic sulfide complex on ZnS and PbS consistent with the $\text{As}_3\text{S}_3(\text{SH})_3$ trimer postulated for sulfidic solutions. This complex was unstable in the presence of oxidizing agents and synchrotron light quickly converted it to As(V), which was largely retained by the surface.

The sorption of arsenic(III) by acid treated spent bleaching earth, an industrial waste produced during the bleaching of crude palm oil was studied to examine the possibility of utilizing this material in water treatment systems [138]. Maximum adsorption occurred at $\text{pH} 9.0$. The adsorption capacity was 0.46 mmol/g . The column studies were also carried out to simulate water treatment processes. The capacity values obtained in column studies were found to be greater than the capacity values obtained in batch studies. NO_3^- , SO_4^{2-} , Cl^- , Br^- did not affect the adsorption of As(III) significantly.

2.2.3. Soils and constituents

2.2.3.1. Soils. Arsenate [As(V)] adsorption–desorption kinetics were reported on Olivier loam, Sharkey clay, and Windsor sand followed by arsenic release using successive dilutions [139]. The As(V) retention rate was initially rapid followed by gradual or slower retention behavior with increased reaction time. A multireaction model (MRM) described the sorption kinetics of As(V) on Olivier loam and Windsor sand. The model also predicted As(V) desorption kinetics for both soils. As(III) and As(V) adsorption on three arid-zone soils from California (Wasco, Fallbrook, and Wyo) was examined at varying As concentrations, pHs, and ionic strengths [140,141]. Chromatographic speciation of As(III)/(V) revealed that the three soils contained low levels of background As(V). Oxidation of added As(III) to As(V) was not detected below $\text{pH} 8$ in soil suspensions during 16-h adsorption. However, As(III) oxidation was detected at high pHs. The soil with the highest Fe levels and clay (Wyo) had the highest affinity for both As(III) and As(V). This soil displayed adsorption behavior similar to pure ferric oxide. As(V) adsorbed more strongly than As(III) under most conditions. However, a pH-dependent reversal in the relative affinity of As(III) and As(V) took place in these soils at low As surface coverage.

The removal and fixation of As(III) and As(V) from water by soil/bentonite mixtures was examined to develop reliable clay liners for waste landfill sites [142]. Either Masatsuchi soil (weathered granite) or Murram soil (pumice) was used as the liner's main body. Wyoming bentonite clays were mixed with each of these soils because of its superior impermeability. More arsenic was removed by Masatsuchi soil without any pH buffer. Both soils exhibited highest As(V) and As(III) adsorption in the pH ranges of 3–6.5 and 7–9.5. Due to the different source and iron loadings, no consistency was obtained in the sorption capacities.

2.2.3.2. Sand. A variety of treated and coated sands were employed for arsenic remediation [143–147]. Sand coated with iron oxide had more pores and a high specific surface area [596]. Manganese greensand (MGS), iron oxide-coated sand (IOCS-1 and IOCS-2) and an ion-exchange (Fe^{3+} form) resin columns were used for dimethylarsinate removal from tap water [148]. Batch studies of IOCS-2 demonstrated an organic arsenic adsorption capacity of $8 \mu\text{g/g}$ IOCS-2. Higher bed volumes (585 BV) and high arsenic removal capacity ($5.7 \mu\text{g}/\text{cm}^3$) were achieved by this resin versus the other adsorbents. Poor performance was observed with MGS and IOCS-1. Recently, Nguyen et al. [146] synthesized iron coated sponge (IOCSp) for As(III) and As(V) removal. Each gram of IOCSp adsorbed about $160 \mu\text{g}$ of arsenic within 9 h. Iron oxide-coated sand was also investigated by Joshi and Chaudhuri [149]. A home unit was designed for the arsenic removal from water. Lo and coworkers [596], also reported the adsorption of heavy metal ions including arsenic on iron coated sand.

Viraraghavan et al. [150] examined manganese greensand and iron oxide-coated sand for arsenic remediation from drinking water. Manganese greensand was effective for removing arsenic to $< 25 \mu\text{g/L}$ [151]. Iron addition was necessary to achieve an effluent arsenic level of $25 \mu\text{g/L}$ in the manganese greensand filtration system. Iron oxide-coated sand (IOCS) exhibited a high adsorption capacity ($136 \mu\text{g/L}$). Another study [152] achieved $285 \mu\text{g/g}$ of arsenic removal on iron oxide-coated sand. Sulfate-modified iron oxide coated sand (SMIOCS) was also used for As(III) and As(V) removal [153,154]. SMIOCS was prepared by coating BaSO_4 and Fe on quartz sand. The maximum As(V) removal was obtained in acidic pHs [154] while maximum As(III) removal was obtained at $\text{pH} 7\text{--}9$ [153]. Gupta et al. [129,130] utilized both iron oxide-coated and uncoated sands for As(III) removal. The maximum Langmuir adsorption capacity of As(III) onto coated sand was five times higher ($28.57 \mu\text{g/g}$) than that onto uncoated sand ($5.63 \mu\text{g/g}$) at $\text{pH} 7.5$ in 2 h. Rapid oxidation of As(III) to As(V) followed by As(V) sorption onto the biogenic manganese oxide surfaces was examined [155,156]. A “family filter” using iron-coated sand was developed for arsenic removal in rural areas of developing countries [143].

Single and multicomponent adsorption of copper, chromate, and arsenate (CCA) onto iron oxide-coated sand (IOCS) was examined by [157]. Copper and arsenate were strongly adsorbed or formed inner-sphere surface complexes with the IOCS surface. Chromate was weakly adsorbed or formed an outer-sphere surface complex. Copper adsorption slightly increased in presence of arsenate but was not affected by chromate. Arsenate adsorption was not affected by the presence of copper and/or chromate. Chromate adsorption increased in the presence of copper by the combination of electrostatic effects and possible surface-copper-chromate ternary complex formation. Arsenate significantly decreased chromate adsorption due to competition for adsorption sites and electrostatic effects. A triple-layer model (TLM) described adsorption of copper, chromate, and arsenate in single-solute systems.

Arsenate was removed from aqueous solutions by coprecipitation with ferrihydrite under conditions in which the Fe/As ratio of 12 held constant, while supersaturation with the iron oxide

precipitate is controlled by iron concentration and pH [158]. Higher supersaturation ratios were required to achieve a given level of arsenic removal at pH 7 at pH 3.5.

Fe-treated activated carbon, Fe-treated gel beds (FeGB) and iron oxide-coated sand were explored for As(III) and As(V) removal [159]. Iron oxide-coated sand was the most effective for As(III) and As(V) removal. As(V) sorption decreased slightly but As(III) remained stable when the pH value was increased from 5 to 9. Aluminum-loaded coral limestones were used for the removal of As(III) and As(V) from aqueous solution [160]. As(III) and As(V) adsorption was almost independent of the initial pH over a wide range (2–11). The adsorption capacity of this treated coral limestone was 150 $\mu\text{g/g}$ for As(V).

Arsenic retention on natural red earth (NRE) was examined as a function of pH, ionic strength, and initial arsenic loading using both macroscopic and spectroscopic methods [161,162]. This NRE is considered as an iron coated sand. Adsorption isotherms were conducted at pH ~ 5.5 for As(III) and As(V) in 0.01 M NaNO_3 at 25 °C for 5 g/L NRE system. The initial As(III) or As(V) concentrations varied between $\sim 10^{-5}$ and $\sim 10^{-4}$ M. Sorption maximum, was observed at ~ 0.173 of As(V) and ~ 0.308 mM of As(III). As(V) showed strong affinity for NRE surface sites versus As(III).

2.2.3.3. Clay minerals. Clay minerals are hydrous aluminum silicates, sometimes with minor amounts of iron, magnesium and other cations (http://en.wikipedia.org/wiki/Clay_minerals). Clays have structures similar to the micas and therefore form flat hexagonal sheets. Typical clay minerals are kaolinite, illite and montmorillonite (http://en.wikipedia.org/wiki/Clay_minerals).

Clay minerals and oxides are widespread and abundant in aquatic and terrestrial environments. Finally divided clay minerals and oxides exhibit large surface areas. Clay minerals and oxides adsorb the cationic, anionic, and neutral metal species. They can also take part in the cation- and anion-exchange processes. Their sorption capacities, cation- and anion-exchange properties and binding energies vary widely. Studies of arsenate and arsenite removal from water by oxides and clay minerals have appeared [134,135,140,141,163–168].

Arsenic remediation by clay-rich limestone from the Soyatal formation in Zimapán, Mexico was studied and compared with other rocks from the region [163]. The experimentally contaminated water (0.6 mg As/L) was reacted with various rocks from the Zimapán region. All rocks decreased the aqueous arsenic concentration below detection limits (<0.030 mg/L) in any contaminated waters that had been reacted with the Soyatal Formation. A rock: water weight ratio of 1:10 reduced the aqueous arsenic concentration in native water from 0.5 to <0.030 mg/L. The calcareous shale of the Soyatal formation contains kaolinite and illite. Both minerals adsorbed arsenic.

Adsorption of arsenate on kaolinite, montmorillonite and illite [169] and arsenite [140,141] on kaolinite, illite, montmorillonite, and amorphous aluminum hydroxide ($\text{am-Al}(\text{OH})_3$) were investigated as a function of pH, and competing anions. The As(V) concentration (6.7×10^{-7} M), the amount of suspended clay (2.5 g/L) and the ionic strength (0.1 M NaCl) were held constant [169]. Distinct As(V) adsorption maxima

(0.15–0.22 mmol As(V) kg^{-1}) occurred at approx. pH 5.0 for kaolinite, 6.0 for montmorillonite and 6.5 for illite. When both As(V) and phosphate were present at equimolar concentrations (6.7×10^{-7} M), As(V) adsorption decreased slightly. In contrast, As(V) adsorption substantially decreased in binary As(V)/phosphate systems when the phosphate concentration was 10 times greater than As(V) (e.g., 6.7×10^{-6} M). The presence of Mo at 6.7×10^{-7} M (10 times greater concentration than As(V)) caused only slight decreases in As(V) adsorption because the Mo adsorption maxima occurred at pH < 4 . The constant capacitance surface complexation model [91] was applied to As(V)/phosphate adsorption data and then used to predict As(V) adsorption at varying phosphate concentration. As(III) adsorption was also compared with As(V) adsorption [140,141]. Surface complexation modeling was used to describe As(III) and As(V) adsorption on these four minerals. Without these clays present, alkaline solutions (pH > 9) caused homogeneous oxidation of As(III) to As(V). In addition, the recovery of As which had been adsorbed on clay minerals showed that heterogeneous oxidation of As(III) to As(V) had occurred on kaolinite and illite surfaces.

As(V) adsorption onto a crude, purified, Ca-exchanged kaolinite and two kaolinites coated with humic acids having different nitrogen contents were carried out by Saada et al. [168]. The adsorption of each humic acid followed by As(V) adsorption onto the humic acid–kaolinite complexes was studied. These coatings influenced As adsorption. The solid/liquid partition coefficient (R_d) values for both complexes were greater at low initial As concentrations than R_d for the crude kaolinite. Higher initial As concentrations decreased the R_d values of the humic acid-coated kaolinites until they were the same as the crude kaolinite R_d values. This suggested that adsorption first occurred on the HA sites followed by the remaining kaolinite sites once the coating's sites were saturated. The humic acid amine groups played an important role in As adsorption onto organic matter due to their protonation at pH 7. Amorphous Al and Fe oxides, kaolinite, montmorillonite, and illite were studied as a function of pH for As(III) and As(V) removal [597]. Arsenate adsorption on these oxides and clays was maximum at low pH and decreased at pH > 9 for Al oxide, pH > 7 for Fe oxide and pH > 5 for the clays. Arsenite adsorption exhibited parabolic behavior with adsorption maxima at \sim pH 8.5 for all these materials. There was no competitive effect of the presence of equimolar arsenite on arsenate adsorption while a competitive effect of equimolar arsenate on arsenite adsorption was obtained only on kaolinite and illite in the pH range 6.5–9. The constant capacitance model was fitted to arsenate and arsenite adsorption envelopes, providing values of the intrinsic As surface complexation constants which were then used in modeling to predict competitive arsenate and arsenite adsorption.

Arsenate adsorption mechanisms at allophane–water interfaces was investigated [164]. X-ray absorption analyses suggested that As(V) formed bidentate binuclear surface species on aluminum octahedral structures which were stable for 11 months. Solubility calculations and powder XRD analyses indicated no evidence of crystalline Al–As(V) precipitates. Overall, macroscopic and spectroscopic studies suggested that the As(V)

adsorbed at allophane–water interface by ligand-exchange reactions between As(V), surface-coordinated water molecules and hydroxyl and silicate ions.

The goethite (surface area 103 m²/g) prepared from the oxidation of ferrous carbonate from double decomposition of ferrous sulfate doped with sodium lauryl sulfate and sodium carbonate was also used for arsenate removal [170]. Adsorption capacity of ~5 mg/g (pH 5.0) was achieved.

Arsenic adsorption on clay minerals including natural metakaoline, natural clinoptilolite-rich tuff, and synthetic zeolite in both untreated and Fe-treated forms was investigated [171]. Sorption capacity of Fe^{II}-treated sorbents increased significantly versus the untreated material (from about 0.5 to >20.0 mg/g, which represented more than 95% of the total As removal). The changes of Fe-bearing particles, occurring in the course of the treating process and subsequent As sorption, were investigated by the diffuse reflectance spectroscopy and the voltammetry of microparticles. Hydrotalcite (HT), a clay material, was used for the remediation of As(III) and As(V) from drinking [172,173]. Percolation through HT of water containing 500–1000 µg/L As (levels often found in As-contaminated well water) produced leachate with As levels well below 10 µg/L. The ‘spent’ HT was converted into valuable a phosphatic fertilizer that would have an insignificant effect on soil arsenic levels, thereby reducing the overall cost of manufacture and distribution [172,173].

2.2.3.4. Zeolites. Zeolites have been received increasing attention for pollution control as standard components in wastewater treatment [174]. Both ion exchange and adsorption properties of zeolites have been used for the selective separation of cations from aqueous solution. Zeolites are crystalline, hydrated aluminosilicates of alkali and alkaline earth cations, having infinite, three-dimensional structures [175]. They can lose and gain water reversibly and exchange constituent cations without change in structure. There are more than 30 natural zeolites known, but only seven (mordenite, clinoptilolite, chabazite, erionite, ferrierite, phillipsite, and analcime) occur in sufficient quantity and purity to be exploited.

The diffusion, adsorption and ion exchange in zeolites have been reviewed [176–178]. Kesraoui-Ouki et al. [174] reviewed natural zeolite utilization in metal effluent treatment applications. Dewatered zeolites produce channels that can adsorb molecules small enough to access the internal cavities while excluding larger species. Zeolites, modified by ion exchange, can be used for adsorption of different metal ions according to requirements and costs.

Batch removal of arsenate and arsenite from water on iron-treated activated carbon and natural zeolite was studied [179]. Molecular sieves, Faujasite (13X) and Linde type A (5A), were also compared. Activated carbon removed ~60% of arsenate and arsenite while Chabazite removed ~50% of the arsenate and ~30% of the arsenite. Arsenate removal by iron-treated activated carbon and clinoptilolite best fit the Langmuir model while arsenate removal by iron-treated chabazite and arsenite removal by activated carbon, chabazite, and clinoptilolite gave better Freundlich model fits.

Elizalde-González et al. [180,181] reported aqueous arsenic sorption by natural zeolites, volcanic stone, cactaceous powder CACMM and clinoptilolite-containing rocks. The content of the zeolitic phases was: 55% clinoptilolite + 35% erionite in ZMA (Maxican, Sonora), 40% clinoptilolite + 30% mordenite in ZME (Maxican, Oaxaca) and 55% clinoptilolite + 30% mordenite in ZH [181]. Sample ZME had the lowest clinoptilolite content. Other minor mineral phases present in the zeolites were feldspars (anorthoclase and albite), quartz, cristobalite, calcite, mica and tosudite (Na_{0.3}Al₆(Si,Al)₈O₂₀(OH)·10.4H₂O). Amounts included ±10% tosudite in ZMA, ±15% feldspars + quartz + cristobalite in ZMS (Maxican, San Luis Potosí), ±10% calcite and ±20% feldspars + mica + quartz in ZMT (Maxican, Puebla) and ZME, ±15% quartz in ZH (Hungarian). Two samples also exhibited mordenite and erionite zeolitic phases. Each zeolitic sample (ZMA, ZME, ZMS, ZMT) in the 0.1–4 mg/L concentration range removed more H₂AsO₄⁻ than H₃AsO₃ at equivalent arsenic concentrations. The addition of iron did not significantly improve the removal efficiency. The saturation capacity of the tuffs was inversely related to the silicon dioxide content and directly to the iron content in the acid-washed zeolite.

The adsorption of As(V) from drinking water by an aluminum-loaded Shirasu-zeolite (Al-SZP₁) was slightly dependent on the initial pH over a wide range (3–10) [182]. Al-SZP₁'s ability to adsorb As(V) was equivalent to that of activated alumina. Competing arsenite, chloride, nitrate, sulfate, chromate, and acetate ions had little affect but phosphate greatly interfered with the adsorption. A ligand-exchange mechanism between As(V) ions and surface hydroxide groups on Al-SZP₁ was presumed. The adsorbed As(V) ions were desorbed by 40 Mm aqueous NaOH. An iron-conditioned zeolite was prepared and used for arsenic removal from groundwater at pH 7.8 and temperature 145 °C [183].

2.2.4. Oxides

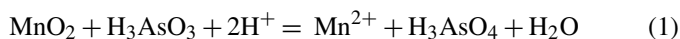
As discussed before Clay minerals and oxides are widespread and abundant in aquatic and terrestrial environments. Studies of arsenate and arsenite removal from water by oxides and clay minerals have appeared [140,141,163–168,134,135].

2.2.4.1. Single oxides.

2.2.4.1.1. Birnessite or manganese dioxide. Manganese oxides minerals have important environmental chemistry uses. They readily oxidize and adsorb many reduced species such as As(III) [184–191]. Synthetic birnessite has been extensively investigated because it is representative of many naturally occurring manganese oxides [184–189,192–194]. Na- and K-substituted birnessites are phylломanganates, possessing layered sheet structures with edge-sharing Mn octahedral [192,193]. These nearly vacancy-free layers of Mn octahedral are influenced by Jahn-Teller distortion when Mn(III) substitutes for Mn(IV). An ordered distribution of Mn(III)-rich rows, interlayer counterions (Na⁺ or K⁺), and octahedral vacancies complete the crystal structure [192,193]. The average empirical formula for sodium birnessite has been given as Na_{0.333}(Mn_{0.722}⁴⁺Mn_{0.222}³⁺Mn_{0.055}²⁺)O₂ [193], indicating

a partial negative charge per unit cell. Moore et al. [184] found that the O/Mn ratio for most synthetic birnessites is near 2. For simplicity, the birnessite chemical formula was simplified to MnO_2 .

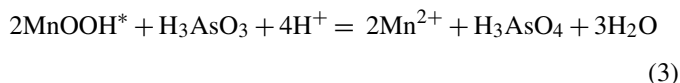
The chemical mechanism of As(III) heterogeneous oxidation by birnessite is emerging [184–189]. Oxidation of As(III) by synthetic birnessite is coupled with the reductive dissolution of the MnO_2 surface. This results in the release of both As(V) and Mn(II) to solution at low pH [184–189]. The net stoichiometry of the reaction is



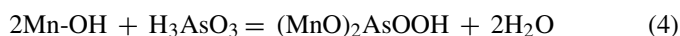
Recently Nesbitt et al. [185] demonstrated by X-ray photoelectron spectroscopy (XPS) that the oxidation of As(III) by the synthetic 7 Å birnessite surface proceeded by a two-step pathway, involving the reduction of Mn(IV) to Mn(III):



where MnOOH^* is a Mn(III) intermediate reaction product. This reaction is followed by the reaction of As(III) with MnOOH^* :



An additional reaction could include the adsorption of As(V) by the MnO_2 surface:



where Mn-OH represents a reactive hydroxyl group on the MnO_2 surface and $(\text{MnO})_2\text{AsOOH}$ represents the As(V) surface complex. Considerable effort has yielded the reaction mechanisms of As(III) with MnO_2 compounds but very little information is available about the formation of As(V) complexes after the oxidation of As(III).

The oxidation of arsenite (As(III)) by manganese oxide is an important reaction in both the natural cycling of As and in developing remediation technology for lowering As(III) the concentration in drinking water. Manning et al. [190,191] studied arsenic removal using synthetic birnessite (MnO_2), employing both a conventional stirred reaction apparatus and extended X-ray absorption fine structure (EXAFS) spectroscopy to investigate the reactions of As(III) and As(V). As(III) is oxidized by MnO_2 followed by the adsorption of the As(V) reaction product onto the MnO_2 solid phase. The As(V)–Mn interatomic distance determined by EXAFS analysis was 3.22 Å for both As(III)- and As(V)-treated MnO_2 . This was evidence for the formation of As(V) adsorption complexes on MnO_2 crystallite surfaces. The most likely As(V)– MnO_2 complex is a bidentate binuclear corner-sharing (bridged) complex occurring at MnO_2 crystallite edges and interlayer domains. In the As(III)-treated MnO_2 systems, reductive dissolution of the MnO_2 solid during the oxidation of As(III) caused an increase in the adsorption of As(V) when compared with As(V)-treated MnO_2 . This suggested that As(III) oxidation caused a surface alteration, creating fresh reaction sites for As(V) on MnO_2 surfaces. This also points out a potential advantage of using

MnO_2 surfaces to treat waters contaminated by both As(III) and As(V).

Arsenic removal from drinking water by monocomponent fixed-bed adsorption of phosphate and arsenate using two natural manganese oxides was investigated by Ouvreard et al. [195,196]. The concentration variations at the column outlet were deduced simply by conductivity and pH measurements. These macroscopic-scale data enabled phenomenological information to be obtained on the surface reactions involved. Two behaviors were found. When surface complexation alone occurred, adsorption isotherms could be rapidly and accurately measured by a series of column experiments. However, when surface complexation was coupled with anion exchange, the system was far more complex. Direct detection of arsenate breakthrough from the conductivity and pH signals was no longer possible. Column experiments were conducted using different particle sizes and flow rates [196]. Transport was influenced by non-linear adsorption and intraparticle diffusion. Total adsorption capacity varied with the flow rate and particle size. Results were interpreted using the effective diffusivity of arsenate in the grain as a single adjustable parameter by a transport model including the Langmuir adsorption and mass transfer. Diffusivities between 0.6 and $7.0 \times 10^{-11} \text{ m}^2 \text{ s}^{-1}$ were calculated which included intraparticle diffusion. These values were close to published pore diffusivities of arsenate in activated alumina grains. This simple model succeeded in predicting the arsenate breakthrough points at different flow rates with a single value of the effective diffusivity.

2.2.4.1.2. Biogenic manganese oxides. Indigenous iron- and manganese-oxidizing bacteria catalyzed the oxidation of dissolved Mn(II) in ground waters. These bacteria were subsequently removed by filtration which created coating on the filter media [197]. Arsenic simultaneously present in the groundwater was removed by sorption. This method is an alternative treatment option for the removal of low-level arsenic concentrations (35 and 42 $\mu\text{g/L}$ for As(III) and As(V), respectively). Rapid As(III) oxidation was observed prior to removal by sorption onto the biogenic manganese oxide surfaces. This rate of As(III) oxidation (0.23 min^{-1}) was significantly higher than literature rates reported for abiotic As(III) oxidation by manganese oxides. Thus, bacteria play an important role in both the As(III) oxidation and the generation of reactive manganese oxide surfaces for the removal of dissolved As(III) and As(V). The following reaction sequence occurred: (a) oxidation of Mn(II) to Mn(IV) and Fe(II) to Fe(III), (b) oxidation of As(III) to As(V), (c) precipitation of manganese(IV) oxides, (d) abiotic oxidation of As(III) by manganese(IV) oxides, and (e) As(V) sorption by manganese(IV) oxides, where steps a and b were biotic and steps c–e were abiotic. Phosphates present at concentrations of $\sim 600 \mu\text{g/L}$ had an adverse effect on As(III) removal (competitive adsorption) and reduced the overall removal efficiency from 80% to 30%. However, phosphates did not affect the oxidation of As(III).

2.2.4.1.3. Activated alumina. Activated alumina (AA), prepared by thermal dehydration of aluminum hydroxide, has a high surface area and a distribution of both macro- and micropores. The United Nations Environmental Program agency

(UNEP) classified AA adsorption among the best available technologies for As removal from water. Arsenic(V) sorption occurs best mostly between pH 6.0 and 8.0 where AA surfaces are positively charged. As(III) adsorption is strongly pH dependent and it exhibits a high affinity towards AA at pH 7.6 [198]. Arsenic adsorption on AA has received substantial attention [9,198–206,216]. Activated Al_2O_3 has been effectively used for arsenic removal from drinking water at pH 5.5 at the Fallon, Nevada, Naval Air Station [38].

Singh and Pant [198,207,208] removed arsenites from water with AA and iron oxide-impregnated AA [209]. The effect of adsorbent dose, pH, and contact time were investigated. As(III) removal was strongly pH dependent. Both Freundlich and Langmuir adsorption isotherms were fit by the experimental data. As(III) adsorption on AA was exothermic [198] while it is endothermic [209] with impregnated activated alumina. Adsorption kinetics were governed by a pseudo first order rate equation in both cases. The adsorption capacity of iron oxide-impregnated AA (12 mg/g) [209] was much higher than AA (7.6 mg/g) [198] (Table 5). Column studies were also performed and the parameters necessary for the design of fixed-bed reactors were evaluated [207,208]. The equilibrium and kinetics of As(III) and As(V) adsorption on AA were also investigated by Lin and Wu [203]. A pore diffusion model, coupled with the observed Freundlich or Langmuir isotherm equations, was used to interpret the experimental adsorption kinetic curve for arsenite at one specific condition. This pore diffusion model predicted the experimental data for As(III) and As(V) at different initial arsenic concentrations, activated alumina grain sizes, and pHs.

Conventional AA has ill-defined pore structures, low adsorption capacities and exhibits slow kinetics [201]. An ideal adsorbent should have uniformly accessible pores, a three-dimensional pore system, a high surface area, fast adsorption kinetics and good physical and/or chemical stability. To achieve these features, mesoporous alumina (MA) with a large surface area (307 m^2/g) and uniform pore size (3.5 nm) was prepared and tested for arsenic removal [201]. A sponge-like interlinked pore system was developed through a post-hydrolysis. The resulting MA was insoluble and stable at pH 3–7 and its adsorption kinetics were rapid. The maximum As(V) uptake by MA was seven times higher [121 mg of As(V)/g and 47 mg of As(III)/g] than that of conventional AA (Table 5). This adsorbent's surface area did not greatly influence the adsorption capacity. The key factor is a uniform pore size. More than 85% of the adsorbed arsenic desorbed in less than 1 h using 0.05 M NaOH.

Arsenate adsorption was also achieved on amorphous aluminum hydroxide [210] while the use of commercially available activated alumina for the design and operation of point-of-use treatment system for arsenic removal was also reported [211].

Manganese supported on activated alumina (MAA), prepared by calcining (400 °C) manganese acetate-impregnated activated alumina, was a more effective medium for As(III) and As(V) removal from groundwater than activated alumina (AA) [212]. Fixed-bed studies suggested that MAA was more

effective than AA in removing As(V), As(III), and As(III) and As(V) simultaneously from groundwater. Down flow column tests (bed depth 200 mm; bed flow-through time 20 min; influent arsenic 1.0–0.6 mg/L As(III) and 0.4 mg/L As(V)), established the breakthrough bed volumes. At the World Health Organization's drinking water arsenic guideline of 0.01 mg/L, breakthrough bed volumes were 580 As(V), 550 As(III), and 485 both As(III) and As(V) using AA and 825 As(V), 770 As(III), and 695 both As(III) and As(V) for MAA.

Arsenic removal on an adsorbent prepared by precipitation of $\text{Fe}(\text{OH})_3$ onto Al_2O_3 exhibited a breakthrough capacity of 0.10 mg of As/g adsorbent at 0.05 mg As/L [213]. Adsorbents for As(III) and As(V) removal from drinking water were developed by granulating porous Al_2O_3 , TiO_2 and their mixtures, followed by precipitation of $\text{Fe}(\text{OH})_3$ onto these surfaces [214]. Adsorption was carried out under both static and dynamic conditions. The adsorbents coated with amorphous $\text{Fe}(\text{OH})_3$ were superior to uncoated for both As(III) and As(V) removal (Table 5). Changing the initial pH of the solution from 6.0 to 8.5 increased As(III) adsorption and decreased As(V) adsorption.

Hlavay and Polyak [215] precipitated $\text{Fe}(\text{OH})_3$ on the surface of activated Al_2O_3 supports *in situ*. The Fe content of the AA was 0.31% m/m (56.1 mmol/g) having $\text{pH}_{\text{zpc}} = 6.9$. The total capacity was 0.12 mmol/g. The adsorbent can be used for binding of both anions and cations by varying the pH. If $\text{pH}_{\text{eq}} < \text{pH}_{\text{zpc}}$, anions are sorbed on the $\text{Fe}(\text{OH})_3/\text{Al}_2\text{O}_3$ surface through surface- OH^{+2} and -OH groups. The pH of the isoelectric points for these adsorbents (pH_{iep}) were 6.1 for As(III) and 8.0 for As(V). The Langmuir adsorption capacities for As(III) and As(V) are reported in Table 5.

As(III) removal on alumina was compared to removal on activated carbon at 30 °C and pH 7.4 [216]. The isotherm for As(III) on activated alumina was typically of Brunauer Type-I but the activated carbon sorption capacity increased with increase in concentration. The Langmuir isotherm model best represented the data for As(III) on activated alumina and the Freundlich model in activated carbon. Adsorption capacity of As(III) on activated carbon was higher than activated alumina.

2.2.4.1.4. Titanium dioxide. Nanocrystalline titanium dioxide's (TiO_2) ability to remove arsenate and arsenite and to photocatalytically oxidize As(III) was evaluated [217]. The nanocrystalline TiO_2 was prepared by hydrolysis of a titanium sulfate solution [218]. Batch adsorption and oxidation experiments were conducted with TiO_2 suspensions in 0.04 M aqueous NaCl. The challenge water contained phosphate, silicate, and carbonate competing anions. The adsorption followed pseudo-second-order kinetics. The TiO_2 was effective for As(V) removal at pH < 8. Maximum As(III) removal occurred at pH ~ 7.5. The adsorption capacity of nanocrystalline TiO_2 of As(V) and As(III) was much higher than that for fumed TiO_2 (Degussa P25) and granular ferric oxide. More than 0.5 mmol/g of As(V) and As(III) was adsorbed by the TiO_2 at an equilibrium arsenic concentration of 0.6 Mm (Table 5). Competing anions had a moderate effect on the adsorption capacities of the TiO_2 for As(III) and As(V) at a neutral pH. In the presence of sunlight and dissolved oxygen, As(III)

(26.7 Mm or 2 mg/L) completely photocatalytically oxidized within 25 min to As(V) in a 0.2 g/L TiO₂ suspension. The adsorption mechanism for As(III) and As(V) on nanocrystalline titanium dioxide was also established using electrophoretic mobility (EM) measurements, Fourier transform infrared (FTIR) spectroscopy, extended X-ray absorption fine structure (EXAFS) spectroscopy, and surface complexation modeling [219]. The adsorption of As(V) and As(III) decreased the point of zero charge of TiO₂ from 5.8 to 5.2, suggesting the formation of negatively charged inner-sphere surface complexes for both arsenic species. The EXAFS study indicated that As(V) and As(III) formed bidentate binuclear surface complexes as evidenced by an average Ti–As(V) bond distance of 3.30 Å and Ti–As(III) bond distance of 3.35 Å. The FTIR bands caused by vibrations of the adsorbed arsenic species remained at the same energy levels at different pH values. Consequently, the surface complexes on TiO₂ maintained the same non-protonated speciation at pH values from 5 to 10, and the dominant surface species were (TiO)₂AsO₂[−] and (TiO)₂AsO[−] for As(V) and As(III), respectively.

Adsorption of As(V) and As(III) on commercially available titanium dioxide (TiO₂) suspensions (Hombikat UV100 and Degussa P25) was investigated versus pH and initial adsorbate concentration [220]. More As(V) and As(III) adsorb onto Hombikat UV100 particles than onto Degussa P25 particles. Adsorption of As(V) was >As(III) onto TiO₂ suspensions at pH 4 while the capacity of As(III) was greater at pH 9. The Langmuir and Freundlich isotherm equations interpreted the adsorption of arsenic onto TiO₂ suspensions.

Jing et al. [155,156] investigated the adsorption mechanisms of monomethylarsonic acid [CH₃AsO(OH)₂] (MMA) and dimethylarsinic acid [(CH₃)₂AsO(OH)] (DMA) on nanocrystalline titanium oxide (TiO₂) using X-ray absorption spectroscopy (XAS), surface charge and zeta potential measurements, adsorption edge, and surface complexation modeling. XAS data demonstrated that MMA and DMA formed bidentate and monodentate inner-sphere complexes with the TiO₂ surface, respectively. The charge and zeta potential behaviors of TiO₂ as a function of ionic strength suggested that the point of zero charge (PZC) and the isoelectric point of TiO₂ were identical at pH 5.8. Adsorption of MMA and DMA on TiO₂ shifted the isoelectric point to pH 4.1 and 4.8, respectively. This indicated the formation of negatively charged surface complexes occurred. The experimental data was explained by the charge distribution multi-site complexation model [221] with the triple plane option [221] under the constraint of the XAS evidence. The monolayer adsorption capacity was not calculated.

Bang et al. [222] studied a novel granular titanium dioxide (TiO₂) for groundwater arsenic removal. More arsenate was adsorbed than arsenite on TiO₂ at pH 7.0. The adsorption capacities for As(V) and As(III) were 41.4 and 32.4 mg/g TiO₂, respectively. This TiO₂ had similar adsorption capacities for As(V) and As(III) (approximately 40 mg/g) using simulated Bangladesh groundwater. Nakajima et al. [223] also investigated the combined use of TiO₂-photocatalyst and an adsorbent with high adsorption ability for As(V), under photo-irradiation. An effective oxidation of As(III) into As(V) was obtained when

As(III) solution was stirred and irradiated by sunlight or xenon lamp in the presence of TiO₂ suspension resulting 89% As(V) removal after 24 h.

Jezeque and Chu [224] investigated titanium dioxide for pentavalent arsenate removal from water. Adsorption isotherms measured at pH 3 and 7 generally followed the Langmuir model. The maximum uptake capacity ranged from 8 mg/g at pH 3 to 2.7 mg/g at pH 7. Addition of phosphate resulted in a significant reduction in arsenate adsorption.

2.2.4.1.5. Lanthanum hydroxide. Lanthanum hydroxide (LH), lanthanum carbonate (LC), and basic lanthanum carbonate (BLC) remove As(V) from aqueous solutions [225]. These lanthanum compounds were effective at a concentration of <0.001 M. Dissolution was appreciable at initial pH values <4.3, <4.3, and <4.0 for LH, LC and BLC, respectively. Arsenic removal followed first-order kinetics in the neutral pH range, and the order of the rate constants was LH > LC > BLC. The optimum pH range was 3–8 for LH, 4–7 for LC, and 2–4 for BLC. Two arsenic uptake mechanisms were proposed: (i) adsorption by the exchange of CO₃^{2−} and (or) OH groups with arsenic ions in neutral to alkaline pH where La does not dissolve and (ii) precipitation of insoluble lanthanum arsenate, LaAsO₄, in acidic pHs.

2.2.4.1.6. Ferrihydrite/iron hydroxide/iron oxides. Iron oxides, oxyhydroxides and hydroxides, including amorphous hydrous ferric oxide (FeO-OH), goethite (α-FeO-OH) and hematite (α-Fe₂O₃), are promising adsorbents for removing both As(III) and As(V) from water [111,226–229]. Amorphous Fe(O)OH has the highest adsorption capability since it has the highest surface area. Surface area is not the only criterion for high removal capacities of metal ions and other mechanisms (ion exchange, precipitation) play an important role. Most iron oxides are fine powders that are difficult to separate from solution after. Therefore, the EPA has proposed iron oxide-coated sand filtration as an emerging technology for arsenic removal at small water facilities [230,231]. Another shortcoming of amorphous FeOOH is its tendency to form low surface area crystalline iron oxides during preparation, greatly reducing its As removal capacity. Different types of ferrihydrites, iron hydroxide and iron oxides were prepared and tested. Some recent studies are now discussed.

Swedlund and Webster [232] synthesized ferrihydrite and studied its use to remove As(III) and As(V) from water. Synthesis was performed by rapidly raising the pH from ~2.0 to 8.0 for different concentrations of Fe(NO₃)₃·9H₂O and 0.1 M NaNO₃ by the addition of NaOH (0.1–5.0 M). The oxide formed as a red/brown, loose gelatinous precipitate, aged for 18–24 h prior to adsorption experiments. X-ray diffraction of the freeze-dried product showed two broad characteristic ferrihydrite peaks. The specific surface area (N₂-BET) of the freeze-dried product was 205 m² g^{−1}. Silicic acid (H₄SiO₄) and ferrihydrite interact both by adsorption and by polymerization. Silicic acid has a significant effect on the adsorption of the oxyanions of arsenic. The adsorption constants for H₄SiO₄, As(V), and As(III) adsorption onto ferrihydrite have been determined using the diffuse layer model (DLM). Silicic acid probably adsorbs as a monomer when the total Si to Fe mole ratio was <0.1. The inhibitory effect of

H₄SiO₄ on As(III) and As(V) adsorption was accurately modeled using the DLM. DLM predicted almost all of the observed effect of H₄SiO₄ on As(III) and As(V) adsorption by considering only H₄SiO₄ adsorption. Thus, H₄SiO₄ adsorption inhibits As adsorption to a greater degree than H₄SiO₄ polymerization.

Granular ferric hydroxide (GFH) was investigated for arsenic removal from natural water [233]. The application of GFH in test adsorbers demonstrated high treatment capacity of 30,000–40,000 bed volumes before an arsenic concentration of 10 µg/L was exceeded in the adsorber effluent. The sorption capacity was 8.5 g/kg (Table 5).

Badruzzaman et al. [234] evaluated porous granular ferric hydroxide for arsenic removal in potable water systems. Granular ferric hydroxide (GFH) is a highly porous (micropore volume ~0.0394 cm³ g⁻¹, mesopore volume ~0.10 cm³ g⁻¹) adsorbent with a BET surface area of ~235 m² g⁻¹. The pseudo-equilibrium (18 days of contact) arsenate adsorption capacity at pH 7 was 8 µg As/mg dry GFH at a liquid phase arsenate concentration of 10 µg As/L. The homogeneous surface diffusion model described the column reactor data. A non-linear relationship ($D_s = 3.0 \times 10^{-9} \times R_p^{1.4}$) was obtained between D_s and GFH particle radius (R_p). D_s values ranged from 2.98×10^{-12} cm² s⁻¹ for the smallest GFH mesh size (100 × 140) to 64×10^{-11} cm² s⁻¹ for the largest GFH mesh size (10 × 30).

Raven et al. [235] compared the adsorption behavior of arsenite and arsenate on ferrihydrite [(Fe³⁺O₃·0.5(H₂O))]. At relatively high As concentrations, adsorption was almost complete in a few hours and arsenite reacted faster than arsenate with the ferrihydrite. However, arsenate adsorption was faster at low As concentrations and low pH. Adsorption maxima at pH 4.6 (pH 9.2 in parentheses) of 0.60 (0.58) and 0.25 (0.16) mol_{As}/mol_{Fe}⁻¹ were achieved for arsenite and arsenate, respectively. Overall arsenite and arsenate have strong affinities for ferrihydrite, and arsenite retained in much larger amounts than arsenate at high pH (approximately >7.5) or at high As concentrations in solution.

The high arsenite retention was due to the fact that ferrihydrite was transformed to a ferric arsenite phase and not simply adsorbed at the surface.

Binding of arsenite to ferric hydroxide using several density functional theory methods was investigated by Zhang et al. [236]. Calculated and experimentally measured As–O and As–Fe bond distances confirmed that arsenic formed bidentate and monodentate corner-sharing complexes with Fe(III) crystalline. Edge-sharing As(III) complexes were less energetically favored and had As–O and As–Fe distances that deviated from experimentally measured values more than corner-sharing complexes.

Adsorption and desorption of methylarsonic acid [CH₃AsO(OH)₂], methylarsonous acid [CH₃As(OH)₂], dimethylarsinic acid [(CH₃)₂AsO(OH)], dimethylarsinous acid [(CH₃)₂AsOH], arsenate [AsO(OH)₃], and arsenite [As(OH)₃] on iron oxide minerals (goethite and 2-line ferrihydrite) was studied by Lafferty and Loeppert [237]. Monomethylarsonous acid and monomethylarsonic acid were not appreciably retained by goethite or ferrihydrite within the pH range from 3 to 11 but arsenite was strongly adsorbed to both iron oxides.

Monomethylarsonic acid and arsenate were adsorbed in higher amounts than dimethylarsinic acid on goethite and ferrihydrite in the pH range 3–10 while dimethylarsinic acid was adsorbed only at pH values below 8 by ferrihydrite and below 7 by goethite. All arsenic compounds were desorbed more efficiently by phosphate than sulfate. Methyl substitution favored a drop in adsorbed arsenic at low arsenic concentrations and the easier release of arsenic from the iron oxide surface.

Roberts et al. [227] studied the arsenic removal by oxidizing naturally present Fe(II) to iron(III) (hydr)oxides by aeration. These iron(III) species precipitated with adsorbed arsenic. Application of Fe(II) instead of Fe(III) was advantageous, because the dissolved oxygen used for oxidation of Fe(II) causes partial oxidation of As(III). Furthermore iron(III) (hydr)oxides formed in this way have higher sorption capacities. Multiple additions of Fe(II) followed by aeration further increase As(III) removal. A competitive coprecipitation model with As(III) oxidation was established.

Lee et al. [238] investigated the stoichiometry, kinetics, and mechanism of arsenite [As(III)] oxidation and coagulation by ferrate [Fe(VI)]. As(III) was oxidized to As(V) (arsenate) by Fe(VI), in a 3:2 [As(III):Fe(VI)] stoichiometry. As(III) oxidation with Fe(VI) was first-order in both reactants. The observed second-order rate constant at 25 °C decreased non-linearly from 3.54×10^5 to 1.23×10^3 M⁻¹ s⁻¹ as pH increased from 8.4 to 12.9. An oxygen transfer mechanism was proposed for the oxidation of As(III) by Fe(VI). Fe(VI) was very effective in arsenic removal from water at a low Fe(VI) dose level (2.0 mg/L). In addition, the combined use of a small amount of Fe(VI) (below 0.5 mg/L) and Fe(III) as a major coagulant was effective for removing arsenic. Akaganeite [Fe³⁺_{7.6}Ni_{0.4}O_{6.4}(OH)_{9.7}Cl_{1.3}] in either fine powder (nanocrystals) or granular forms can also be used to remove As(V) from water [239,240]. Akaganeite powder was prepared by FeCl₃ hydrolysis in aqueous solutions and precipitation using ammonium carbonate. Increasing ionic strength increased in removal efficiency. Granular akaganeite was less effective than powder. Column sorption studies were conducted and the bed-depth-service time model by McKay [241] was applied. As(V) removal by akaganeite β-FeO(OH) nanocrystals was also reported [242]. Arsenic removal increased with increasing temperature and the Langmuir adsorption capacities were compared (Table 5).

Cumbal et al. [243] reported the preparation of two classes of iron-containing polymer-supported nanoparticles for As(III) and As(V) removal: (i) hydrated Fe(III) oxide (HFO) dispersed on a polymeric ion-exchange resin and (ii) magnetically active polymeric particles. The high surface area to volume ratios of these nanoscale particles favored both sorption and reaction kinetics. However, extremely high-pressure drops, prevented fixed-bed column applications. *In situ* reactive barriers and in similar flow-through applications were not possible. These also lack durability and mechanical strength.

Electrochemical peroxidation (EPC) at steel electrodes with H₂O₂ is an emerging As(III) remediation technology [244]. ECP effectively removed arsenic from the aqueous solutions, with >98% of the As(III) adsorbed on solid hydrous ferric oxides. Removal was complete within 3 min, independent of the initial

aqueous pH (3.5–9.5). In the absence of H_2O_2 more As(III) was adsorbed by solid state iron at pH 9.5 than at 3.5 (2600 $\mu\text{g/L}$ versus 1750 $\mu\text{g/L}$). The optimal operating conditions were $\text{pH} < 6.5$, $[\text{H}_2\text{O}_2] = 10 \text{ mg/L}$ and a process time $\leq 3 \text{ min}$.

Westerhoff et al. [245] studied arsenate adsorption on porous granular ferric hydroxide (GFH) using rapid small-scale column tests (RSSCT). These RSSCTs captured changes in water quality (source water and pH) and operational regimes (e.g., EBCTs) and could be used to aid in the selection and design of arsenic removal media for full-scale treatment facilities. Adsorption densities from column tests (q_{column}) were calculated at the point in the breakthrough curve when arsenate equaled 10 $\mu\text{g/L}$ in the column effluent. At 2.5 min contact time, a model water (pH 8.6) had q_{column} values of 0.99–1.5 mgAs/Ggfh versus only 0.02–0.28 mgAs/Ggfh in natural groundwater with a comparable pH and contact time. The differences were attributed to the silica, phosphate, vanadium, and other competing adsorbable inorganics in the groundwater. At pH 7.6–7.8, q_{column} values from proportional diffusivity-RSSCTs in the three natural waters were comparable (1.5 mgAs/Ggfh) and higher than constant diffusivity-RSSCT q_{column} values (0.57 mgAs/Ggfh) in these same waters. Redman et al. [246] studied the influences of natural organic matter (NOM) samples on the sorption of arsenic onto hematite. The effects of arsenic on the sorption of six NOM were obtained using conditions and concentrations relevant to natural freshwater environments. Four formed aqueous complexes with arsenate and arsenite. The extent of complexation varied with the NOM origin and increased as the cationic metal (primarily Fe) content increased. In addition, every NOM sample showed active redox behavior toward arsenic species. Thus, the NOM may greatly influence redox as well as complexation speciation of arsenic in freshwater environments. Incubation of NOM with As and hematite, dramatically delayed completion of sorption equilibrium and diminished both arsenate and arsenite sorption. Furthermore, all NOM samples displaced sorbed arsenate and arsenite when NOM and As were introduced sequentially. Similarly, arsenic species displaced sorbed NOM in significant quantities.

The influence of laboratory controlled aging on the stability of arsenate coprecipitated with hydrous ferric oxide (HFO) was studied [247] to assess (1) the transformation rate of HFO to more stable products, (2) the extent to which arsenate was stabilized within more crystalline iron (hydr)oxides, and (3) the rate of arsenate stabilization. The rate of arsenate stabilization approximately coincided with the rate of HFO transformation at pH 6 and 40 °C. Extraction data and X-ray diffraction results confirmed that hematite and goethite were the primary crystalline products. HFO transformation was significantly retarded at, or above, arsenate loadings of 29.4 mg As/kg HFO. However, HFO transformation proceeded rapidly to hematite (XRD studies) for arsenate solid loadings of 4.2 g and 8.4 g mg As/kg HFO. Thus, a baseline time scale was provided of solid recrystallization processes that stabilizes arsenate coprecipitated with iron (hydr)oxides.

Arsenate and dimethylarsinate (DMA) adsorption kinetics on goethite ($\alpha\text{-FeOOH}$) were investigated versus pH and inert electrolyte concentrations Zhang and Robert [248]. Adsorp-

tion kinetics were described and compared using Elovich plots. Arsenate and DMA desorption was achieved by increasing the suspension's pH from 4.0 to 10.0 or 12.0. The effect of replacing a hydroxyl group with a methyl group on the adsorption behavior of As(V) was studied using the adsorption edges, the influence of ionic strength on adsorption, and the effect of adsorption on the goethite's zeta potential [249]. The affinity of three arsenic species to the goethite surface in the pH range of 3–11 decreased in the order of $\text{AsO}_4 = \text{MMA} > \text{DMA}$. Replacement of two hydroxyl groups by methyl groups made the affinity of arsenic to goethite smaller, while replacing one hydroxyl had a small effect on the arsenic adsorption on goethite. The low affinity of DMA to goethite was due to the formation of monodentate rather than bidentate surface complexes [249].

Ranjan et al. [250] synthesized hydrous ferric oxide, for arsenic sorption. As(V) sorption strongly depended on the system's concentration and pH, while As(III) sorption was pH insensitive. As(III) required less contact time to attain equilibrium. SO_4^{2-} , PO_4^{3-} , and HCO_3^- competed poorly with As(III) sorption. Exhausted columns were regenerated with 5 M NaOH. The columns were recycled five times. A natural oxide sample consisted Mn-mineral and Fe-oxides was used for As(III) and As(V) removal. Maximum adsorption capacities of 8.5 and 14.7 mg/g were obtained for As(V) and As(III), respectively, at pH 3.0 in 100 $\mu\text{g/L}$ to 100 mg/L concentration range [594].

Adsorption of arsenite and arsenate versus pH was studied on goethite, amorphous iron hydroxide, and clay pillared with titanium (IV), iron(III), and aluminum(III) synthesized from a bentonite with a montmorillonitic-pillared fraction [251]. These sorbents were characterized by XRD, FTIR, BET, DTA/TGA, surface acidity, and zetametry. Arsenate adsorption was favored in acidic pH, whereas maximum arsenite adsorption was obtained at $4 < \text{pH} < 9$. The pillared clays were damaged at $\text{pH} > 10$ and adsorption decreased. Equilibration times and adsorption isotherms were also determined for arsenite and arsenate at each matrix's auto-equilibrium pH. Amorphous iron hydroxide had the highest removal capacities for arsenate and arsenite (Table 5). Arsenate adsorption capacities were similar for goethite and iron- and titanium-pillared clays but those for arsenite were different. Desorption from iron- and titanium-pillared clays was achieved with efficiencies of >95 and $\sim 40\%$, respectively. Stamer and Nielsen [252] developed a fluid-bed technology where arsenic is bound to continuously generated ferric oxyhydroxide in the form of dense granules with arsenic content of 50 g As/Kg or more. Inexpensive ferrous sulfate precipitant is used combined with stoichiometric addition of hydrogen peroxide. The residence time in the reactor was 10 min.

The adsorption of As(V) present in concentrations ranging from 100 to 750 $\mu\text{g/L}$ over the pH range of 4–9 on ferric hydroxide (GFH) was investigated [228]. The adsorption decreased as the pH of the solution increased, and optimal adsorption was at pH 4. The competitive effect of phosphate on the uptake of arsenate at pH 4 by GFH was also investigated. GFH had a greater affinity for arsenate adsorption compared to phosphate.

Arsenic adsorption on magnetite (Fe_3O_4) nanoparticles was conducted by Mayo et al. [253]. The effect of Fe_3O_4 particle size

on the adsorption and desorption behavior of both As(III) and As(V) was reported. As the particle size was decreased from 300 to 12 nm the adsorption capacities for both As(III) and As(V) increased nearly 200 times.

A fibrous polymeric/inorganic sorbent material was synthesized and used for arsenic remediation [254]. The sorbent included polymer filaments inside which nanoparticles of hydrated Fe(III) oxides have dispersed. The functional groups of this weak-base anion exchanger allowed high (1.0–1.4 mmol/g) and fairly uniform Fe(III) loading. While hydrous ferric oxide (HFO) microparticles provide a high sorption affinity toward dissolved arsenic species, the fibrous polymeric matrix guarantees excellent hydraulic and kinetic characteristics in fixed beds. This hybrid sorbent, FIBAN-As, was selective to both arsenites and arsenates and exhibited excellent arsenic removal efficiency without any pH adjustment or pre-oxidation of the influent. In addition, As(III) sorption was not suppressed in presence of SO_4^{2-} , Cl^- , HPO_4^{2-} at pH typical for drinking waters.

In an important contribution, Yavuz et al. [255] applied magnetic separations at very low magnetic field gradients (<100 T/m) for point-of-use water purification and the simultaneous separation of complex mixtures. High surface area and monodisperse magnetite (Fe_3O_4) nanocrystals (NCs) responded to low fields in a size-dependent fashion. The particles did not act independently in the separation but rather reversibly aggregated through the resulting high-field gradients present at their surfaces. Using the high specific surface area of Fe_3O_4 NCs that were 12 nm in diameter, the mass of waste associated with arsenic removal from water was reduced by orders of magnitude. In addition, the size dependence of magnetic separation permitted mixtures of 4- and 12-nm-sized Fe_3O_4 NCs to be separated by the application of different magnetic fields.

Iron oxide was immobilized onto a naturally occurring porous diatomite [256]. This immobilized iron oxide was reported to be an amorphous hydrous ferric oxide (HFO). The sorption trends of Fe (25%)-diatomite for both arsenite and arsenate were similar to those of HFO, reported earlier [257]. The optimum pH was 7.5. Arsenic sorption capacities of Fe (25%)-diatomite were comparable to or higher than those of HFO. The pH-controlled differential column batch reactor (DCBR) and small-scale column tests demonstrated that Fe (25%)-diatomite had high sorption speeds and high sorption capacities compared to those of a conventional sorbent (AAFS-50) that is known to be the first preference for arsenic removal performance in Bangladesh. ArsenXnp, a hybrid sorbent consisting of nanoparticles of hydrous iron oxide distributed throughout a porous polymeric bead was utilized for arsenic remediation from drinking water [258]. Arsenic was removed due to the interaction with the nanoscale hydrous iron oxide surfaces rather than the anion-exchange groups associated with the polymeric substrate. Anions such as sulfate, chloride, or bicarbonate did not interfere.

Two separation processes were used for arsenic remediation [259]. In the first process arsenic selective removal using hybridized IX-fibers having dispersed hydrated ferric oxide (HFO) nanoparticles was achieved. Anion-exchanger-supported HFO particles offered a high arsenic removal capacity (less than 10% of influent arsenic broke through after 30,000 bed

volumes). Hybrid fibers were regenerable by 2% NaOH and 2% NaCl and also capable of simultaneous removal of both As(V) and As(III). The second process involved the environmentally benign removal of hardness. This process used harvested snowmelt (or rainwater) sparged with carbon dioxide as the regenerant. The bulk of carbon dioxide consumed during regeneration remains sequestered in the aqueous phase as alkalinity. For both treatment strategies, IX-fibers form the heart of the process.

2.2.4.1.7. Zirconium oxide. Exchange behavior of hydrated ZrO (HZO) (100–200 mesh) was investigated to selectively remove As(III) and As(V) from water [260]. As(V) adsorbed more readily than As(III). The interference of foreign ions such as Ca^{2+} , Mg^{2+} , Fe, Cu, HCO_3^- , Cl^- , NO_3^- , SO_4^{2-} , and PO_4^{3-} on As(III) and As(V) adsorption were also examined. HZO was reusable for As removal from drinking water.

2.2.4.2. Mixed oxides.

2.2.4.2.1. Mixed rare earth oxides. Raichur and Penvekar [261] reported the use of a mixed rare earth oxide adsorbent (La_2O_3 44%; CeO_2 2.0%; Pr_6O_{11} 10.5%; Nd_2O_3 36.5%; Sm_2O_3 5.0%) for As(V) removal from aqueous solution. More than 90% of the adsorption took place within the first 10 min with a kinetic rate constant of 3.5 mg/min. The Langmuir sorption capacity was calculated (Table 5).

2.2.4.2.2. Portland cement. Kundu et al. [262] utilized a hardened Portland paste cement having SiO_2 (21%), CaO (63%), Al_2O_3 (7%), Fe_2O_3 (3%), MgO (1.5%), surface area (15.38 m^2/g) and pore volume 0.028 cm^3/g as an arsenic adsorbent. Arsenate removal exceeded (~95%) that of arsenite (~88%). The iron oxide treated cement was also used for As(III) and As(V) removal [263–267,556]. The Langmuir adsorption capacities for As(III) and As(V) at neutral pH were 0.67 and 6.43 mg/g, respectively (Table 5).

2.2.4.2.3. Soil aquatic sediments. Aquifer material from the San Antonio-El Triunfo mining area was tested for ground water arsenic removal [268]. Quartz, feldspar, calcite, chlorite, illite, and magnetite/hematite were all present in the aquifer material. A maximum of ~80% arsenite was adsorbed. The adsorption isotherm at pH 7 indicated saturation of surface sites at high solute concentrations. The point of zero charge (PZC) for the adsorbent was ~8 to 8.5 (PZC for iron oxyhydroxides = 7.9–8.2). MICROQL and MINTEQA2 geochemical models suggested that As was mostly adsorbed by iron oxyhydroxides surfaces in the natural environment.

As(III) and As(V) adsorption and mobility (desorption) on an oxisol, and its main mineral constituents was investigated by Ladeira and Ciminelli [269]. Goethite in this soil was the most efficient arsenic adsorbent, retaining 12.4 mg/g of As(V) and 7.5 mg/g of As(III). Gibbsite also adsorbed considerable As (4.6 mg/g of As(V) and 3.3 mg/g of As(III)). Adsorption on kaolinite was negligible (<0.23 mg/g for As(V) and As(III)). Arsenic desorption varied with the arsenic oxidation state, the adsorbents and the leaching solutions. While only 1–2% max. of As(V) was released from the loaded samples, 32% of the As(III) leached. The highest As(III) leaching occurred into solutions

containing sulfate ions. Oxisol and goethite were superior to gibbsite for As immobilization. As(V) was mainly adsorbed as an inner-sphere complex while As(III) may be adsorbed as either inner or outer-sphere neutral complexes.

2.2.4.2.4. Sea sediments. As(III) and As(V) adsorption on polymetallic sea nodules was reported by Maity et al. [270]. Major elemental constituents of sea nodules were MnO₂ (31.8%), Fe₂O₃ (21.2%) and SiO₂ (14.2%) with traces of Cu, Ni, Co, Ca, K, Na and Mg and loss on ignition (LOI) 20.3%. Mineral phases associated with sea nodules were primarily non-crystalline and extremely hygroscopic in nature. Crystalline phases identified were silica ($d=3.35$) and a shifted β -MnO₂ ($d=3.20$) phase. The optimum (Langmuir) As(III) loading was 0.74 mg/g at 0.34 mg/L while that of As(V) was 0.74 mg/g at 0.78 mg/L. As(III) adsorption was not influenced by anions except for PO₄³⁻ but cations influenced its adsorption significantly. As(V) adsorption, conversely, is influenced by anions and not by cations. Both As(III) and As(V) adsorptions exhibited very little desorption over pH 2–10.

2.2.4.3. Hydroxides. Arsenic adsorption/desorption behavior on aluminum and iron (oxyhydr)oxides has been extensively studied but very few studies are available describing arsenic adsorption/desorption behavior on bimetal Al:Fe hydroxides. Recently, Masue et al. [271] studied the influence of the Al:Fe molar ratio, pH, and counterion (Ca²⁺ versus Na⁺) on arsenic adsorption/desorption to/from coprecipitated Al:Fe hydroxides. Adsorbents were developed by initial hydrolysis of mixed Al³⁺/Fe³⁺ salts to form coprecipitated Al:Fe hydroxide products. At a Al:Fe molar ratio of 1:4, Al³⁺ was largely incorporated into the iron hydroxide structure to form a poorly crystalline bimetal hydroxide; however, at higher Al:Fe molar ratios, crystalline aluminum hydroxides (bayerite and gibbsite) were formed. Approximately equal As(V) adsorption maxima were observed for Fe hydroxide and 1:4 Al:Fe hydroxide while the As(III) adsorption maximum was greater with the Fe hydroxide. As(V) and As(III) adsorption decreased with further increases in the Al:Fe molar ratio. As(V) exhibited strong affinity to Fe hydroxide and 1:4 Al:Fe hydroxide at pH 3–6. Adsorption decreased at pH > 6.5; however, the presence of Ca²⁺ compared to Na⁺ as the counterion enhanced As(V) retention by both hydroxides. There was more As(V) and especially As(III) desorption caused by added phosphate ions with an increase in Al:Fe molar ratio.

2.2.5. Hydrotalcites

Hydrotalcites have the structural formula [M_{1-x}^{II}M_x^{III}(OH)₂]^{x+}A_{x/n}ⁿ⁻·mH₂O, where M^{II} and M^{III} denote divalent (e.g., Mg, Ni, and Zn) and trivalent metals (e.g., Al, Fe, and Cr), respectively [272]. Aⁿ⁻ represents interlayer anions, such as NO₃⁻, SO₄²⁻, and CO₃²⁻, and x typically ranges from 0.17 to 0.33. These materials consist of positively charged, brucite-like octahedral layers and a negatively charged interlayer region containing anions and water molecules. The presence of large interlayer spaces and a significant number of exchangeable anions cause, hydrotalcites (as known as LDHs) to be good ion-exchangers and adsorbents. LDHs uptake anions from solution by three mechanisms: (1) adsorption, (2) intercalation by

anion exchange, and (3) intercalation by reconstruction of the calcined LDH structure. The latter phenomenon, known as the “memory effect”, takes place when an LDH, containing interlayer carbonates, is calcined to eliminate most of the interlayer anions followed by rehydration and reconstruction of the layered structure. Anions are incorporated and the LDHs “recover” their original structure. In principle, the potential exists for reuse and recycle of the adsorbent [273].

Adsorption of As and Se from dilute aqueous solutions by both calcined and uncalcined LDH layered double hydroxide was investigated [273]. The adsorption capacity for As(V) was greater than Se(IV) for both calcined and uncalcined LDHs. The adsorption capacities for As(V) and Se(IV) onto the calcined LDH are higher than on uncalcined LDH. Competing ions have a greater effect on Se(IV) uptake than on As(V) uptake.

Bhaumik et al. [274] also employed layered double hydroxide Mg–Al hydrotalcite for arsenic removal. The arsenic removal efficiency was further improved by pretreatment with dilute H₂O₂ to oxidize As(III) to As(V) under acid conditions followed by exchange with hydrotalcite. The solid exchanger was regenerated for reuse with a saturated NaCl solution. Kiso et al. [275] utilized three types of hydrotalcite (HTAL-Cl, HTAL-CO₃-HT-500) for arsenic removal. The HTAL-Cl, which contained intercalated Cl⁻ ions showed high adsorption capacity (105 mg/g) in the neutral pH region. Gillman [172,173] also experimented with hydrotalcite for As(III) and As(V) removal from water containing 500–1000 μ g/L As (levels often found in As-contaminated well water) successfully.

2.2.6. Phosphates

As(III) and As(V) were removed using iron(III) phosphate (amorphous or crystalline) [276]. As(III) oxidation by iron(III) and phosphate substitution by As(V) occur during arsenic sorption. Adsorption capacities were higher for As(III) uptake. Solid dissolution and phosphate/arsenate exchange led to the presence of Fe³⁺ and PO₄³⁻ in solution. Fe³⁺ in solution can oxidize As(III) to As(V). Therefore, various precipitates (such as Fe₃(AsO₄)₂·8H₂O_(s) with Fe²⁺ and FeAsO₄·2H₂O_(s) with Fe³⁺) form containing As(V). As(III) was better removed than As(V) on these ferric phosphates. The maximal adsorption capacity was slightly better for FePO_{4(am)}: 21 mg As(III)/g FePO_{4(am)} and 16 mg As(III)/g FePO_{4(cr)}. As(V), adsorption was similar on both iron phosphates: 10 mg As(V)/g FePO_{4(am)} and 9 mg As(V)/g FePO_{4(cr)}. Crystalline and amorphous FePO₄ exhibited a maximum phosphate release at the highest arsenic adsorption, pointing out the probable exchange between arsenate and phosphate due to their similar ionic radii (AsO₄³⁻: 248 nm; PO₄³⁻: 238 nm). Blank studies without As (i.e., solid dissolution only) gave lower phosphate release (1 mg/L); thus the higher concentration in the case of As(III) points to another phenomenon. As(III) was present as H₃AsO₃⁰; therefore these results suggest As(III) oxidation to As(V) occurs, followed by an arsenate/phosphate exchange. Further, the change in pH during As(III) and As(V) adsorption showed that both have different sorption mechanisms. Isao et al. [277] also studied the adsorption of arsenite and arsenate from aqueous solution by silica gel particles loaded with ferric hydroxide (1–3 wt.% Fe based

on the dry gel). Silica gel loaded with 3.3 wt.% Fe, adsorbed ≤ 0.07 mmol arsenic per g of dry gel.

2.2.7. Metal-based methods

Strong cation-exchange resins, macroporous polymers, chelating resins and biopolymer gels have been used in the preparation of metal-loaded polymers. They are classified here according to that metal. These metal-loaded polymers have then been used to adsorb arsenic [278]. The reader can find good description of various resins used for arsenic remediation in the review by Dambies [278].

2.2.7.1. Zero-valent iron. The use of Fe(0) to remove arsenic has been actively investigated by many groups [190,191,279–293]. The surface area exposed plays a major role in both the adsorption kinetics and capacities. Kanel et al. [294,295] synthesized nanoscale (1–120 nm diameter) zero-valent iron (NZVI) for rapid, first order As(III) and As(V) removal ($k_{\text{obs}} = 0.07\text{--}1.3 \text{ min}^{-1}$) This rate was about 1000 times faster than that of micron-sized iron. Batch experiments determined the feasibility of using NZVI for As(III)/As(V)-contaminated groundwater remediation versus initial arsenic [As(III) or As(V)] concentrations and pHs (pH 3–12). The maximum As(III) adsorption Freundlich capacity was 3.5 mg of As(III)/g for NZVI. Light scattering electrophoretic mobility measurements confirmed a NZVI-As(III) inner-sphere surface complexation mechanism.

Bang et al. [291,292] utilized zero-valent iron filings for arsenic remediation. Arsenic removal was dramatically affected by oxygen content and pH [291]. Arsenate removal by Fe(0) filings was faster than arsenite under oxic conditions. Greater than 99.8% of the As(V) was removed whereas 82.6% of the As(III) was removed at pH 6 after mixing for 9 h. When dissolved oxygen was removed by nitrogen purging, less than 10% of the As(III) and As(V) was removed. High dissolved oxygen content and low solution pH increased the iron corrosion rate. Thus, arsenic removal by Fe(0) was attributed to adsorption onto iron hydroxides generated from Fe(O). The As(III) removal rate was higher than that for As(V) when iron filings (80–120 mesh) were mixed with nitrogen-perged arsenic solutions in the pH range of 4–7 [292]. XPS spectra demonstrated As(III) surface reduction to As(0). As(V) was reduced to As(III) with Fe(0) under anoxic conditions, but no As(0) was detected in solution after 5 days. Arsenic uptake by Fe(0) proceeded by electrochemical reduction of As(III) to insoluble As(0) and adsorption of As(III) and As(V) on surface iron hydroxides formed under anoxic conditions. The removal rates of As(V) and As(III) from water were much higher under air than under the anoxic conditions. As(V) removal was faster than As(III). Adsorption of As(III) and As(V) was rapid on surface ferric hydroxides formed by Fe(0) oxidation by dissolved oxygen.

The potential use of Fe filings to remove monomethyl arsenate (MMA) and dimethyl arsenate (DMA) from contaminated waters was further demonstrated [296]. The affinity of MMA for Fe filings was comparable to that of inorganic arsenate, but lower than that for arsenite. In contrast, less DMA was retained by Fe filings or their corrosion products. The effectiveness of

Fe filings was also demonstrated with a field deployment at a U.S. Superfund site where groundwater is highly contaminated with both organic and inorganic As species. Over the course of 4 months, a 3 L cartridge of Fe filings removed >85% of As contained in 16,000 L of groundwater containing 1–1.5 mg/L total dissolved As, ~30% of which was organic As.

Zero-valent iron mechanisms for arsenate removal from drinking water were also investigated by Farrell et al. [280]. Batch experiments using iron wires suspended in anaerobic arsenate solutions were performed to determine arsenate removal rates as a function of the arsenate solution concentration. Corrosion rates were determined as a function of elapsed time using Tafel analysis. Batch reactor removal kinetics were described by a dual-rate model. Arsenate removal was pseudo-first-order at low concentrations and approached zero-order in the limit of high arsenate concentrations. Arsenate decreased iron corrosion rates as compared to those in a blank 3 mM CaSO₄ electrolyte solutions.

Arsenate removal kinetics from water by zero-valent iron media was investigated to determine iron corrosion rate effects on the rate of As(V) removal [281,282]. As(V) removal in columns packed with iron filings was measured over 1 year of continuous operation. As(V) removal on freely corroding versus cathodically protected iron confirmed that continuous generation of iron oxide adsorption sites and As(V) diffusion through iron corrosion products determined the rates. The presence of 100 $\mu\text{g/L}$ As(V) decreased the iron corrosion rate by up to a factor of 5 compared to a blank electrolyte solution. However, increased As(V) concentrations (100–20,000 $\mu\text{g/L}$) caused no further decrease in the iron corrosion rate. Arsenate removal kinetics ranged between zeroth- and first-order versus the aqueous As(V) concentration.

Recently, modified nanosized zero-valent iron (Fe⁰) particles such as NiFe and PdFe were synthesized by borohydride reduction of nickel and palladium salts on Fe⁰ particles and used for arsenate removal [293]. Increasing the temperature caused an increase in arsenate removal while competing sorption of phosphate and sulfate inhibited arsenate removal.

2.2.7.2. Bimetallic adsorbent. Zhang et al. [297] investigated a Fe–Ce bimetal oxide adsorbent for arsenic removal using X-ray powder diffraction (XRD), transmission electron micrograph (TEM), Fourier transform infrared spectra (FTIR), and X-ray photoelectron spectroscopy (XPS). The bimetal oxide adsorbent exhibited a significantly higher As(V) capacity than the individual Ce and Fe oxides (CeO₂ and Fe₃O₄) prepared by the same procedure. Various mechanisms were proposed based on the results obtained from XRD, FTIR, TEM, and XPS.

2.2.7.3. Metal-chelated ligands. Fryxell et al. [298] reported the synthesis and use of metal-chelated ligands immobilized on mesoporous silica as novel anion binding materials. Nearly complete removal of arsenate and chromate from solutions containing more than 100 mg/L was achieved in the presence of competing anions under a variety of conditions. Anion loading was more than 120 mg (anion)/g of adsorbent. A binding mechanism based on computer modeling was also proposed. First,

Cu(II) ions bonded to ethylenediamine ligands to form surface octahedral complexes on the mesoporous silica. This gave rise to positively charged hosts with three-fold symmetry that match the geometry of tetrahedral anions. The anion binding involved initial electrosteric coordination, followed by displacement of one ligand and direct binding with the Cu(II) center.

Highly ordered mesoporous silica, SBA-15 impregnated with iron, aluminum, and zinc oxides were used for arsenic removal [299]. A 10 wt.% aluminum-impregnated sample (designated to Al₁₀SBA-15) had 1.9–2.7 times greater arsenate adsorption capacities over a wide range of initial arsenate concentrations and a 15 times greater initial sorption rate at pH 7.2 than activated alumina. Surface complexation modeling of arsenate adsorption edges, at different pH values, indicated that the monodentate surface-bound complex (AsO₄²⁻) was dominant in Al₁₀SBA-15. Conversely, bidentate surface complexes of HASO₄ and AsO₄⁻ were dominant on activated alumina at pH 7.2. Al₁₀SBA-15 had a single fast-rate initial adsorption step at pH 7.2, while activated alumina had both fast and slow arsenate adsorption steps.

Fe(III)-Octolig-21 composite was prepared from dried Octolig-21 and used for arsenic remediation [300]. Octolig-21 is an immobilized ligand containing (polyethyleneamino) groups bound to a silane that is covalently bound to silica gel. A stream of ingoing water containing 50 ppb As over a 1 kg composite might last for months before column would lose effectiveness at the flow rate of 5 L/h.

Yoshitake et al. [301] utilized diamino group-functionalized MCM-41 and MCM-48 for arsenate remediation. Fe³⁺, Co²⁺, Ni²⁺, and Cu²⁺ were captured by these diamino moieties. Elemental analyses were consistent with 2:1 and 1:1 coordinations of the ligand to metal cations. The mono-, di-, and triamino-functionalized silica chlorides were denoted by H/N-, H/NN-, and H/NNN-mesoporous silicas, respectively, where mesoporous silica is MCM-41 or MCM-48. The average forms of Fe and Cu on NN-mesoporous silicas were Fe(en)₂ and Cu(en)₂, respectively, while Co²⁺ was mostly bound to one en ligand. Ni²⁺ was adsorbed on unfunctionalized mesoporous silicas, resulting in low N/Ni²⁺ ratios. Fe³⁺ and Co²⁺ were superior to the other cations after complexation on silica, achieving complete removal of As from the solutions as evaluated by K_d. Fe³⁺ and Co²⁺ achieved high adsorption capacities, and selectivities in the solution in the presence of SO₄²⁻ and Cl⁻. The highest adsorption capacity of arsenate, 2.5 mmol/(g of adsorbent), was achieved on Fe/NN-MCM-48, in which each Fe³⁺ bound to an average of 2.7 arsenate anions. The adsorption capacities of M/NN-MCM-48 (M = Fe, Co, Ni, Cu) were much larger than those of M/NN-MCM-41, though the As/M stoichiometries are almost the same.

The adsorption of nitrate, chromium(VI), arsenic(V) and selenium(VI) by a secondary and tertiary amine-modified coconut coir (MCC-AE) has been reported [302]. Batch adsorption-ion-exchange experiments were conducted using 200 mg of MCC-AE, initially containing chloride as the resident anion, and 50 mL of different anion-containing water solutions with varying concentrations. At low pH, SeO₄²⁻ remained as the only divalent anion, while monovalent species H₂AsO₄⁻

and HCrO₄⁻ predominated in their respective exchanging ion solutions. MCC-AE exhibited a preference for Cr₂O₇²⁻ and SeO₄²⁻ compared to the resident Cl⁻ ion. The maximum As(V) adsorption was 0.086 mmol/g versus 0.327, 0.459, and 0.222 mmol/g, for Cr(VI), NO₃⁻ and Se(VI) anions, respectively (Table 5). Comparative adsorption experiments were also conducted using commercial Amberlite IRA-900 quaternary amine chloride anion-exchange resin (exchange capacity of 4.2 mequiv./g). The maximum adsorption of ions in IRA-900 was about 3 times higher for NO₃⁻, 9 times higher for Se(VI), 10 times higher for As(V) and 9 times higher for Cr(VI), than those exhibited by MCC-AE. Differences in the ion-exchange behavior of MCC-AE and IRA-900 were probably due to their different amine functionalities.

2.2.7.4. Cation-exchange resins.

2.2.7.4.1. *Ce(IV) resins.* PHA and IDA (Amberlite IRC-718) chelating polymers were loaded with cerium(IV) chloride at pH 5.65 and 6 [303]. Ce(IV)-Amberlite IRC-718 removed 99% of As(V) from a 374.5 ppm solution at pH 3.25, while Ce(IV)-PHA removed only 81% at pH 2.75.

2.2.7.4.2. *Cu(II) resins.* Cu(II)-loaded sorbents were prepared from two commercially available resins, Amberlite IRC-718 and pyridyl/tertiary ammonium groups (Dowex 2N), by Ramana and Sengupta [304]. Copper loadings were 0.85 and 1.6 mmol/g, respectively. Cu(II)-Dowex 2N removed As(V) in presence of 250 mg SO₄²⁻/L at pH 8.5 where Amerlite IRA-900 was ineffective.

2.2.7.4.3. *Fe(III) resins.* The adsorption of As(III) and As(V) on an iron(III)-loaded chelating resin containing lysine-N^α,N^α-diacetic acid functional groups (Fe-LDA) was investigated [305]. Arsenic(V) was strongly adsorbed at 2–4, while arsenic(III) was moderately adsorbed between pH 8 and 10. Maximum Langmuir sorption capacities of 0.74 mmol/g for As(V) at pH 3.5 and 0.84 mmol/g for As(III) at pH 9.0 were obtained (Table 5). Both As(III) and As(V) were almost quantitatively recovered from the resin with 0.1 mol/L sodium hydroxide. During regeneration, less than 0.1% of the ferric ions are leached into the alkaline solutions.

Peleanu et al. [306] examined an iron-loaded iminodiacetate chelating resin and a silica/iron(III) oxide composite material for As(V) remediation. The composite exhibited a higher As(V) adsorption capacity than the iminodiacetate resin. Exposure of the composite to a magnetic field caused the adsorption of As(V) to change in a complex way. The sorption capacity decreased in acidic conditions when the magnetic field was applied. However, at pH 7.0 the magnetic field intensified As(V) adsorption.

Anionic metal remediation using alginate acid pretreated with Ca²⁺ and Fe(III) was investigated by Min and Hering [307]. Spherical gel beads (2 mm in diameter) were formed by dispensing this biopolymer solution dropwise into 0.1 M CaCl₂. The polycarboxylate Ca²⁺ beads were then washed and equilibrated with 0.1 M FeCl₃ to achieve partial substitution of Fe(III) for Ca²⁺. The resulting Ca-Fe containing beads were effective for As(V) removal. Optimum arsenic removal and stability by these beads was achieved at pH 4. As(V) removal efficiency increased with increasing Fe content. At an initial As(V) con-

centration of 400 $\mu\text{g/L}$, up to 94% removal was achieved at pH 4 after 120 h.

DeMarco et al. [308] studied As(III) and As(V) removal on polymeric/inorganic hybrid particles composed of spherical macroporous cation-exchange polymer beads, containing nanoscale hydrated Fe oxide agglomerates that were uniformly and irreversibly dispersed. The new hybrid ion-exchange sorbent combined excellent mechanical and hydraulic properties of spherical polymeric beads with selective As(III) and As(V) sorption properties at neutral pH without any pre- or post-treatment. Efficient *in situ* regeneration was accomplished with caustic soda and a subsequent short carbon dioxide-sparged water rinse. The new sorbent possesses excellent attrition resistance properties and retained its arsenic removal capacity over several cycles.

Katsoyiannis and Zouboulis [309] modified polystyrene and polyHIPE (PHP) by iron hydroxide coatings. Modified media, capable of removing arsenic from the aqueous stream, led to a residual As concentration below 10 $\mu\text{g/L}$. PolyHIPE (PHP) was the more effective arsenic sorbent. Zouboulis and Katsoyiannis [310] also tested biopolymers (alginate) as sorbent supports, for the removal of arsenic. Alginate, a biopolymer extracted mainly from brown seaweed, is a linear polysaccharide of (1 \rightarrow 4)-linked α -L-guluronate (G) and β -D-mannuronate (M) residues arranged in a non-regular, block-wise pattern along the linear chain. A bed of calcium alginate beads was treated (doped/coated) with hydrous ferric oxides. Three modified alginates viz., calcium alginate beads coated with iron oxides and calcium alginate beads doped and coated with iron oxides were tested. The most efficient was Ca-Fe-doped alginate.

An iron(III)-loaded iminodiacetate resin (LEWATIT TP 207) (168 mg Fe/g resin) was employed and a maximum of 60 mg As/g resin was adsorbed at pH 1.7 [311].

2.2.7.4.4. La(III) resins. Trung et al. [312] reported that muromac A1 chelating resin (Na^+ form) loaded with La(III) effectively preconcentrated very dilute solutions of As(V) and As(III). The muromac A1 chelating resin resembles Chelex-100 and both containing iminodiacetic acid [$-\text{CH}_2-\text{N}(\text{CH}_2-\text{COOH})_2$] functional groups but differs in chelating properties. The La(III)-resin removed between 98% and 100% of As(III) and As(V) between pH 4 and 9.

2.2.7.4.5. Y(III) resin. Arsenite and arsenate ions were removed from aquatic systems by using basic yttrium carbonate [313]. The adsorption of >98% of aqueous arsenite and arsenate ions took place in the pH ranges of 9.8–10.5 and 7.5–9.0, respectively. Arsenate was also removed by precipitation at pH below 6.5 due to dissolution of yttrium carbonate. As(III) and As(V) adsorption increased with temperature. Anions such as Cl^- , Br^- , I^- , NO_3^- and SO_4^{2-} did not interfere. The adsorption mechanism was interpreted in terms of the surface charge and yttrium carbonate ligand orientation.

2.2.7.4.6. Zr(IV) resins. Suzuki et al. [314] loaded a porous polymeric resin (dried Amberlite XAD-7) with monoclinic or cubic hydrous zirconium oxide by incorporating $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ into pores of the spherical polymer beads followed by hydrolysis and hydrothermal treatment of the zirconium salt. Hydrous zirconium oxide deposited inside the larger diameter pores. The adsorption capacity and distribution coefficients for As(III) and

As(V) were determined by batch procedures (Table 5). The hydrous zirconium oxide-loaded resin strongly adsorbed As(V) in the slightly acidic to neutral pH region while As(III) was favorably adsorbed at pH \sim 9–10. The Zr resin was regenerated by treating columns with 1 M NaOH followed by conditioning with a 0.2 M acetate buffer solution. The amount of zirconium leached was negligible during adsorption and regeneration. The column was used repeatedly. Adsorption of Se(VI), Se(IV), As(III), As(V), and methyl derivatives of As(V) onto porous polymer beads loaded with monoclinic hydrous zirconium oxide (Zr-oxide) was also reported by Suzuki et al. [315]. As(III) and As(V) was removed by a porous spherical resin loaded with monoclinic hydrous zirconium oxide [316].

Balaji et al. [317] studied the removal of As(V) and As(III) using a zirconium(IV)-loaded chelating resin with lysine- N^α , N^α diacetic acid functional groups. The synthesis of lysine- N^α , N^α diacetic acid (LDA) chelating resin was carried out using the method described by Yokoyama et al. [318]. The introduction of LDA to polystyrene was carried under N_2 atmosphere with sulfomethylated polystyrene beads, which were prepared with chloromethyl polystyrene resin and dimethyl sulfide. Arsenate ions strongly adsorbed in the pH range 2–5, while arsenite was adsorbed between pH 7 and 10.5. Sorption occurred by complexation of arsenate or arsenite to the Zr lysine- N^α , N^α diacetic acid functional groups. Langmuir sorption capacities of 0.656 mmol/g for As(V) at pH 4.0 and 1.184 mmol/g for As(III) at pH 9.0 were reported (Table 5). Regeneration after As(V) adsorption was achieved using 1 M NaOH. Six adsorption/desorption cycles were performed without a significant decrease in the uptake performance. The adsorption of As(V) was more favorable than that of As(III), due to faster As(V) versus As(III) kinetics. Coexisting ions influence the sorption of As(V) and As(III).

Zirconium (Zr) has been loaded on a fibrous phosphoric acid adsorbent, which had been synthesized by radiation-induced grafting of 2-hydroxyethyl-methacrylate phosphoric acid onto polyethylene-coated polypropylene non-woven fabric [319]. Zirconium reacted with the grafted phosphoric acid in the polyethylene layer an uptake of 4.1 mmol Zr/g. The total As(V) capacity was 2.0 mmol/g adsorbent at pH of 2. Chloride and nitrate interfered with the breakthrough capacity.

Zhu and Jyo [320] reported a Zr(IV)-loaded phosphoric acid chelating resin prepared from a copolymer of divinylbenzene and 2-hydroxy-3-OPO₃H₂-propyl methacrylate (Fig. 3). This was employed as an adsorbent for As(V). Little Zr(IV) leakage was observed within a wide pH range. The maximum As(V)

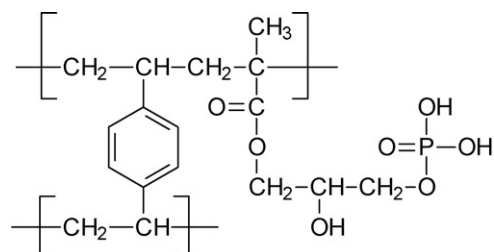


Fig. 3. Chemical structure of the phosphoric acid resin RGP.

capacity was 0.2 mmol/mL of wet resin (0.67 mmol/g of dry resin). Adsorbed As(V) was quantitatively eluted with 0.4 mol/L sodium hydroxide and columns could be repeatedly recycled.

2.2.7.5. Macroreticular chelating resins. The removal and recovery of arsenic from a geothermal power waste solution was accomplished with three macroreticular chelating resins containing mercapto groups [321]. These resins were cured prepared by copolymerizing 2,3-epithiopropyl methacrylate with divinylbenzene (Fig. 4).

The copolymer beads exhibited a high affinity for As(III) ion and high resistance to hot water. Aqueous As(III) was favorably adsorbed on resin columns when a sodium arsenite solution (pH 6.2) containing 3 mg/L of As(III) was passed through at a space velocity of 15 h^{-1} . Adsorbed As(III) eluted with a 2 mol/L sodium hydroxide solution containing 5% of sodium hydrogen sulfide. Recycling was satisfactory. This resin exhibited a high absorption of arsenic from the geothermal power waste solution.

A hydrophilic thiol resin, poly(ethylene mercaptoacetamide), prepared from branched polyethyleneimine (Mwt. 40,000–60,000) and mercaptoacetyl chloride, was examined Styles et al. [322]. This resin had a free mercaptan content of 8.26 mequiv./g and a standard oxidation potential of 0.217 V. It exhibited spontaneous redox sorption of arsenate in acidic media. The removal capacity was 106 mg As/g dry resin at pH 2 for arsenate and 30 mg As/g dry resin at pH 8 for arsenite. In addition to redox sorptions, significant arsenic uptake occurred by thiol complexation and anion exchange on protonated amine sites of the branched polymer. The sorption of both arsenate and arsenite was significantly reduced by NaCl and Na_2SO_4 . Sorbed arsenic was desorbed by 0.2N NH_4OH . The stripped resin, in its oxidized (disulfide) form, is reconverted to the active thiol form by treatment with excess aqueous 10% sodium bisulfite.

2.2.7.6. Anion-exchange resins. Tatineni and Hideyuki [323] studied the adsorption of As(III) and As(V) by titanium dioxide loaded onto an Amberlite XAD-7 resin. This resin was prepared by impregnation of $\text{Ti}(\text{OC}_2\text{H}_5)_4$ followed by hydrolysis with ammonium hydroxide. The resin strongly adsorbed As(V) from pH 1 to 5 and As(III) from pH 5 to 10. Langmuir adsorption capacities of 0.063 mmol/g for As(V) at pH 4.0 and 0.13 mmol/g for As(III) at pH 7.0 were achieved (Table 5).

An anion exchanger (AE) prepared from coconut coir pith (CP) was used for the removal of As(V) from aqueous solutions [324]. The adsorbent (CP-AE), carrying weakly basic dimethylaminohydroxypropyl functional groups, was synthesized by the

reaction of CP with epichlorohydrin and dimethylamine followed by treatment of hydrochloric acid. A maximum removal of 99.2% was achieved for an initial concentration of 1 mg/L As(V) at pH 7.0 and an adsorbent dose of 2 g/L [324]. This adsorbent was tested for As(V) remediation from simulated groundwater. Regeneration of the adsorbent was achieved using 0.1N HCl [324].

Lin et al. [325] studied the transport and adsorption of arsenate by iron-based adsorbent (Bayoxide E33 from Bayer) and one anion-exchange resin (Arsenex from Purolite).

2.2.8. Biosorbents

Biosorption is capable of removing traces of heavy metals and other elements from dilute aqueous solutions. Algae, fungi and bacteria are examples of biomass-derived sorbents for several metals. Such sorbents have produced encouraging results. Gadd [326] and Brierley [327] reviewed how bacteria, fungi and algae take up toxic metal ions. It is important to differentiate *biosorption* or sorption from *bioaccumulation*. Biosorption (or bioadsorption) is a passive immobilization of metals by biomass. Mechanisms of cell surface sorption are independent of cell metabolism; they are based upon physicochemical interactions between metal and functional groups of the cell wall. The microorganism's cell wall mainly consists of polysaccharides, lipids and proteins, which have many binding sites for metals. This process is independent of the metabolism and metal binding is fast [328,329]. Bioaccumulation, in contrast, is an intracellular metal accumulation process which involves metal binding on intracellular compounds, intracellular precipitation, methylation and other mechanisms [328]. Bioaccumulation can also be regarded as a second part of the metal sequestering process by living biomass. Sometimes, it is called *active biosorption* as the opposite to *passive biosorption*. Since it depends on the cell metabolism, it can be inhibited by metabolic inhibitors such as low temperature and lack of energy sources. Biosorption and bioaccumulation differ in kinetics and activation energies ($E_a \sim 21 \text{ kJ/mol}$ for biosorption, which is in agreement with the physical nature of the process and $E_a \sim 63 \text{ kJ/mol}$ for bioaccumulation corresponding to biochemical process) [330,328]. Harvested, non-living biomass can be used for biosorption but not bioaccumulation.

Metal uptake by dead cells takes place by the passive mode. Living cells employ both active and passive modes for heavy metal uptake. Living and dead fungi cell removal of may offer an alternative method for wastewater remediation. The use of fungal biosorbents for heavy metals remediation has been reviewed

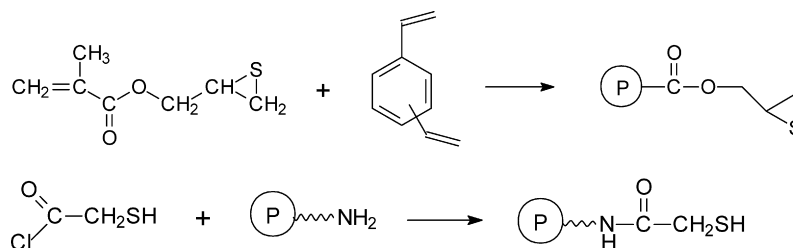


Fig. 4. Preparation of macroreticular chelating resins.

[331]. A range of equilibrium sorption models, and diffusion and sorption models in different reactor systems were reviewed to correlate fungal biosorption experimental data. Fungi are used in many industrial fermentation processes, which could serve as an economical source of biosorbent for arsenic removal. Fungi can also be easily grown in substantial amounts using unsophisticated fermentation techniques and inexpensive growth media. Lignin has also been used for the metal ions remediation [332].

2.2.8.1. Chitin and chitosan. Braconnot first described chitin in 1811, upon isolating a substance he called “fungine” from fungi. The first scientific reference to chitin was taken from the Greek word “Chiton”, meaning a “oat of mail”, for the material obtained from elytra of May beetles [241]. Chitin is the most widely occurring natural carbohydrate polymer next to cellulose. Chitin is a long, unbranched polysaccharide derivative of cellulose, where the C₂ hydroxyl group has been replaced by the acetyl amino group -NHCOCH₃. Chitin is found in the exoskeleton of Crustacea shellfish, shrimp, crabs, insects, etc. 2-Deoxy-2(acetyl-amino) glucose is the primary unit in the polymer chain. These units are linked by β, (1 → 4) glycosidic bonds forming long linear chains with degrees of polymerization from 2000 to 4000. Chitosan is derived from chitin by deacetylation of chitin using concentrated alkali at high temperature. Chitin is first prepared from shells of Crustacea at low-cost by removing other components, such as calcium, and proteins, by treatment with acids and alkalines. Chitin and chitosan are excellent natural adsorbents [333–335] with high selectivities due to the following reasons:

- (1) Large numbers of hydroxyl and amino groups give chitosan high hydrophilicity.
- (2) Primary amino groups provide high reactivity.
- (3) The polymer chains of chitosan provide suitable configurations for efficient complexation with metal ions.

The chemical structures of chitin and chitosan are presented in Fig. 5.

Arsenic and other metal ion adsorption on chitosan, chitin and biomass from *Rhizopus oryzae* was studied McAfee et al. [333]. Removal of arsenic from contaminated drinking water was also studied on a chitosan/chitin mixture [334]. The capacity of the mixture at pH 7.0 was 0.13 μequiv. As/g (Table 5). Dambies et al. [335] studied the sorption of As(V) on molybdate-impregnated chitosan gel beads. The sorption capacity of raw chitosan for arsenic(V) was increased by impregnation with molybdate. The optimum pH for arsenic uptake was ~pH 3. Arsenic sorption was followed by the release of molybdenum. This can be decreased by a pretreatment with phosphoric acid to remove the labile part of the molybdenum. The As sorption capacity, over molybdenum loading, was almost 200 mg As g⁻¹ Mo. The exhausted sorbent regenerated by phosphoric acid desorption. Three sorption/desorption cycles were conducted with only a small decrease in sorption capacity.

Chitosan powder derived from shrimp shells, was converted into bead form and used to remove As(III) and As(V) from water

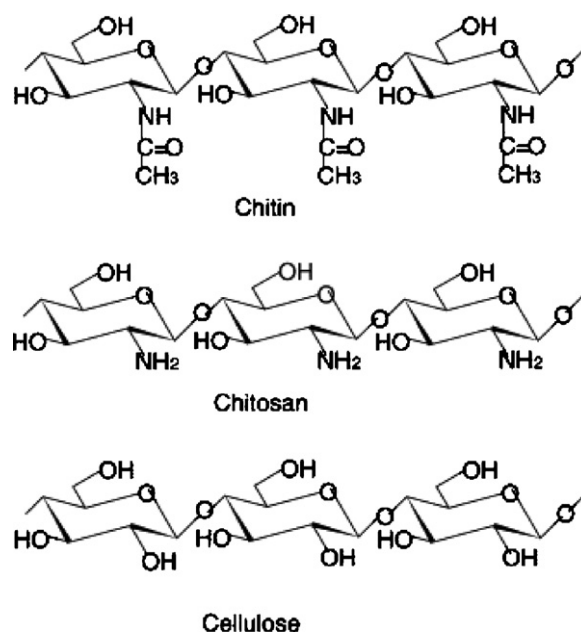


Fig. 5. Structure of chitin, chitosan and cellulose.

in both batch and continuous operations [336]. Furthermore, wastewater containing arsenic discharged from the manufacturing of GaAs supports was also treated in a continuous operation. The optimal pH value for As(III) and As(V) removal was ~5. Adsorption capacities of 1.83 and 1.94 mg As/g bead for As(III) and As(V), respectively, were obtained. Ion coexistence below 50 mg/L did not affect arsenic removal.

2.2.8.2. Cellulose sponge. An open-celled cellulose sponge with anion-exchange and chelating properties (Forager Sponge), prepared by shredding commercial grade 1/2 in. Forager Sponge cubes, was used for arsenic removal [337]. Both unleaded and Fe(III)-loaded sponges were tested. Arsenate was effectively adsorbed by both unleaded and Fe(III)-loaded sponges in the pH range 2–9 (maximum at pH 7). Arsenite was only slightly adsorbed by the Fe(III)-loaded sponge in the pH range 5–10 (maximum at pH 9), while the unleaded sponge was unable to adsorb As(III) in the pH range 5–10. The maximum sorption capacities were 1.83 mmol As(V)/g (pH ~ 4.5) and 0.24 mmol As(III)/g (pH ~ 9.0) for the Fe(III)-loaded adsorbent (Table 5). A 1:1 Fe:As complex was formed for both species. As(V) adsorption selectivity was significantly enhanced by loading Fe(III) into the sponge. Effective As(V) adsorption was demonstrated, even in the presence of high concentrations of interfering anions (chloride, nitrate, sulfate, and phosphate).

Guo and Chen [338] utilized iron oxyhydroxide-loaded cellulose beads for arsenate and arsenite removal from water. The Langmuir adsorption capacities for arsenite and arsenate were 99.6 and 33.2 mg/g at pH 7.0 for beads with an Fe content of 220 mg/mL. Sulfate addition had no effect on arsenic adsorption, whereas phosphate greatly retarded arsenite and arsenate elimination. Silicate moderately decreased the arsenite adsorption, but not that of arsenate. Both batch experiments and column experiments gave higher arsenite removal efficiency than that for

arsenate. The iron oxyhydroxide-loaded beads were effectively regenerated with 2 M NaOH.

As(III) and As(V) removal using orange juice residue and phosphorylated crosslinked orange waste has been considered [339,340]. Orange waste contains cellulose, pectins, hemicellulose, chlorophyll pigments and other low molecular weight compounds like limonene. The active binding sites for metals are thought to be the carboxylic groups of the pectins.

The carboxylic group content of the original orange waste did not bind sufficient iron(III) to adsorb arsenic. Thus, the waste's cellulose content was phosphorylated in order to convert its abundant hydroxyl groups into phosphoric acid groups which have a high affinity for ferric iron [339]. The resulting phosphorylated gel was further loaded with Fe(III) (iron loading capacity of 3.7 mol/kg). Batch and column adsorption studies on this adsorbent found maximum adsorption capacities for As(V) and As(III) of 0.94 and 0.91 mol/kg at their optimum pH values of 3.1 and 10.0, respectively [339] (Table 5).

Ghimire et al. [340] have also phosphorylated both cellulose and orange wastes. The chemically modified adsorbents were then loaded with iron(III) in order to create a medium for arsenate and arsenite chelation. The Fe(III) loading capacity on the gel from orange waste was 1.21 mmol/g compared with 0.96 mmol/g for the gel prepared from cellulose. Arsenite removal was favored under alkaline conditions for both gels. The orange waste gel showed some removal capability even at pH 7.0. Conversely, arsenate removal took place under acidic conditions at pH 2–3 and 2–6 for the cellulose gel and orange waste gel, respectively. The higher Fe(III) loading on the orange waste gel led to greater arsenic removal. Arsenite or arsenate are adsorbed by liquid exchange on the immobilized Fe(III)

centers of the Fe(III)-loaded phosphorylated cellulose and phosphorylated orange wastes (Fig. 6). The ligands involved in such an exchange process may be hydroxyl ions (mechanism 1) or neutral water molecules (mechanism 2) present in the Fe(III) coordination sphere.

Other gels, prepared by the phosphorylation of orange juice residue exhibited 2.68 and 4.96 mol of phosphorous/kg dry gel, respectively [341]. The later, when loaded with ferric iron, exhibited higher adsorption capacities for the removal of oxo anions such as arsenic and selenium. These gels exhibited maximum As(V) adsorption capacities of 0.53 and 0.94 mol/kg dry gel after they were loaded with Fe(III).

Cylindrical lignocellulose pellets (8 mm in diameter and 6 mm in height) with a sodium carboxymethylcellulose (CMC) coating were employed and compared with three well known and currently used industrial adsorbents: ferric oxide, aluminum oxide, and activated charcoal for arsenic remediation [342]. Adsorption capacity of 32.8 mg/g was achieved. The adsorbent was regenerable with dilute NaOH. One ton of Fe(III)-treated adsorbent can be utilized to remove arsenate at toxic levels from drinking water at a cost of ~\$ 3.20/ton plus the cost of media without regeneration.

2.2.8.3. *Biomass*. Various properties of biomass have been reviewed by Mohan et al. [343]. Microfungi have been recognized as promising low-cost adsorbents for heavy metal ion removal from aqueous solutions. A very few studies are reported on the removal of anionic metals including arsenic by fungal organisms [344]. The surface charge of the fungal organisms is normally negative in a pH range of 3–10 [344]. The ability of *Garcinia cambogia*, an indigenous plant found in many parts of

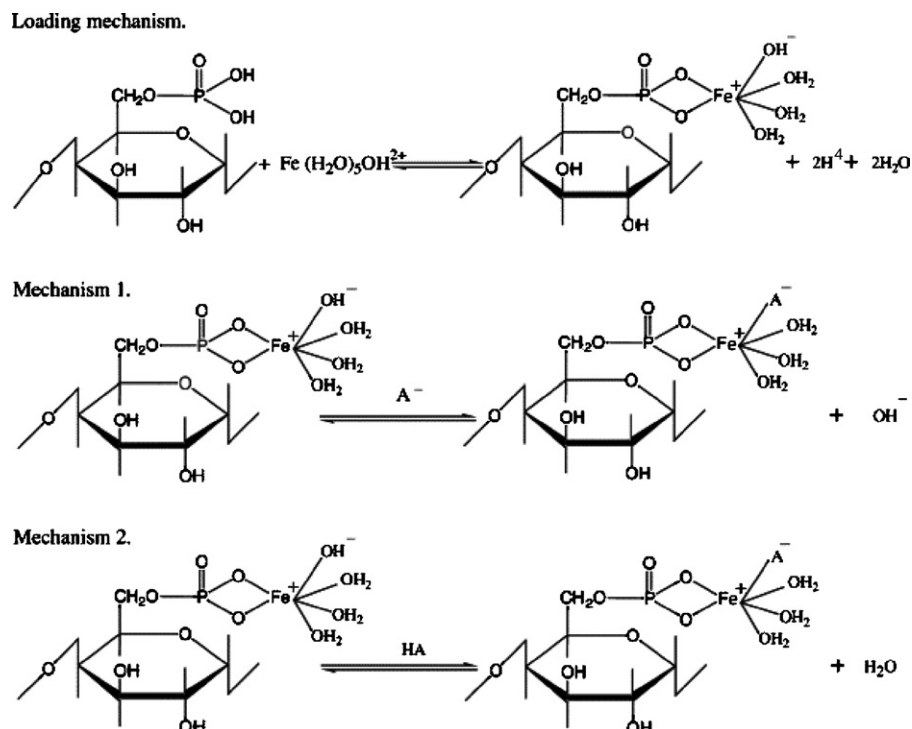


Fig. 6. Adsorption mechanisms of arsenate and arsenite onto iron(III).

India, to remove trivalent arsenic from solution was assessed by Kamala et al. [345]. The As(III) removal capability of fresh and immobilized *G. cambogia* biomass was estimated.

As(III) uptake was not greatly affected by pH with optimal biosorption occurred at around pH 6–8. Common ions such as Ca^{2+} and Mg^{2+} did not inhibit As(III) removal at concentrations up to 100 mg/L, but 100 mg/L of Fe(II) caused a noticeable drop in the extent of As(III) removal. Immobilized biomass columns were recycled five times. Water lettuce (*Pistia stratiotes* L.), an aquatic plant, removed arsenate [346]. Young plants were harvested from a pollution-free pond and hydroponically cultured, effectively absorbed arsenic in a range from 0.25 to 5.0 mg/L. From 22.8% to 82.0% of the As was removed for a biomass loading of 20 g/L at pH 7.0 after 144 h. The sorption capacity was 1.43 mg/g of biomass. *Aspergillus niger*, coated with iron oxide removed 95% of As(V) and 75% of As(III) at a pH of 6. No strong relationship was reported between the surface charge of the biomass and arsenic removal [344].

Ridvan et al. [347] examined the fungus, *Penicillium purpurogenum*, for cadmium, lead, mercury, and arsenic ion removal from water. Heavy metal loading capacity increased with increasing pH under acidic conditions, presumably as a function of heavy metal speciation versus the H^+ competition at the same binding sites. The adsorption of heavy metal ions reached a plateau at \sim pH 5.0. The fungus adsorption capacity for As(III) was 35.6 mg/g (Table 5). Metal ion elution was achieved using 0.5 M HCl. This fungus was recycled through 10 adsorption cycles. The biosorption of cadmium, lead, mercury and arsenic ions by the *Penicillium purpurogenum* fungus has also been reported [348]. Heavy metal loading capacity increased with increasing pH under acidic conditions.

The tea fungus, a waste produced during black tea fermentation, has the capacity to sequester the metal ions from ground water samples [349]. Autoclaved tea fungal mats and autoclaved mats pretreated by FeCl_3 were exploited for As(III), As(V) and Fe(II) removal from ground water samples collected from Kolkata, West Bengal, India. The FeCl_3 -pretreated fungal mats removed 100% of As(III) and Fe(II) after a 30 min contact time. Moreover 77% of As(V) was removed after 90 min. Fungal mat without FeCl_3 was effective for Fe(II) removal from ground water samples.

Lessonia nigrescens, an algae, was also utilized for arsenic(V) removal with maximum adsorption capacities of 45.2 mg/g (pH 2.5); 33.3 mg/g (pH 4.5); and 28.2 mg/g (pH 6.5) in the concentration range of 50–600 mg As(V)/L [350].

Sorghum moss was utilized for the remediation of arsenic from water [351]. The effects of CaCl_2 , MgCl_2 , FeSO_4 , MgSO_4 , $\text{Fe}(\text{NO}_3)_3$ and humic substances on arsenic adsorption were evaluated. Iron slats increased arsenic removal while MgSO_4 decreased the removal by 21%. Arsenic adsorption on sorghum biomass (SB) was also investigated by Haque et al. [352]. Maximum adsorption was achieved at pH 5.0.

Dead fungal biomass from *P. chrysogenum* is an industrial waste with the trade name Mycan. The pretreatment with hexadecyl-trimethylammonium bromide (HDTMA-Br), dodecylamine and a cationic polyelectrolyte was carried out to improve arsenate biosorption [353]. The initial biomass had

a low affinity for metallic anions, whereas modified samples adsorbed significant amounts of arsenic. At pH 3, these modified adsorbents removed 37.9 mg As/g (HDTMA-Br-modified Mycan biomass), 56.07 mg As/g (Magnafloc-modified) and 33.3 mg As/(Dodecylamine-modified) (Table 3). Seki et al. [354] explored methylated yeast biomass for arsenic(V) and Cr(VI) removal. The amounts adsorbed increased with increasing methylation. The amount of adsorbed As(V) peaked at pH 7 and was lower than that of Cr(VI). Cr(VI) and As(V) saturation onto yeast was 0.55 mmol/g.

Teixeira and Ciminelli [355] studied selective As(III) adsorption on waste chicken feathers with a high fibrous protein content. The disulfide bridges present were reduced to thiols by thioglycolate. As(III) adsorption was favored at low pH. Arsenic uptake was 270 μmol As(III)/g of biomass. XANES analyses demonstrated that arsenic is adsorbed in its trivalent state. This is a major advantage over conventional As uptake, which usually requires a previous oxidation to As(V). Each adsorbed As atom was directly bound to three S atoms with estimated As–S distances of 2.26 Å based on EXAFS analyses. Structural similarities existed between the As(III)-biomass complex and that of arsenite ions in the Ars-Operon encoded proteins and phytochelatin.

2.2.8.4. Water hyacinth (*Eichornia crassipes*). The water hyacinth (*E. crassipes*) is a member of the pickerelweed family (Pontederiaceae). The plants vary in size from a few centimeters to over a meter in height [356]. The glossy green, leathery leaf blades are up to 20 cm long and 5–15 cm wide and are attached to petioles that are often sponge-like and inflated. Numerous dark, branched, fibrous roots dangle in the water from the underside of the plant. The water hyacinth family is one of the most productive plant groups on earth. They are also one of the world's most troublesome aquatic plants, forming dense mats that interfere with navigation, recreation, irrigation, and power generation. These mats competitively exclude native submersed and floating-leaved plants. Water hyacinth mats deplete dissolved oxygen and the dense floating mats impede water flow and create good mosquito breeding conditions. The plant is called a "green plague". However, Haris's report [357] published by the Royal Society of Chemistry in the United Kingdom suggests that it may be a natural solution to arsenic water contamination.

Haris and coworkers [357] demonstrated that dried roots of the water hyacinth rapidly reduce arsenic concentrations in water to levels less than the maximum value (10 ppb) for drinking water recommended by the World Health Organization [357]. Water hyacinth plants from a pond in Dhaka, Bangladesh were dried in air and a fine powder was prepared from the roots. More than 93% of arsenite and 95% of arsenate was removed from a solution containing 200 μg of arsenic per L within 60 min of exposure to the powder. The arsenic concentration remaining was less than the WHO drinking water guideline value of 10 $\mu\text{g}/\text{L}$.

Earlier, Misbahuddin and Fariduddin [358] had noted that water hyacinths removed arsenic when placed in arsenic-contaminated water for 3–6 h. The extent of arsenic removal depended on the arsenic concentration present, the amount of

water hyacinth used, the exposure time and the presence of air and sunlight. Contrary to Shaban et al. [357], these authors reported that whole plants were more effective than fibrous roots alone.

Water hyacinths (*E. crassipes*) were used as a pollution monitor for the simultaneous accumulation of arsenic, cadmium, lead and mercury [359]. After 2 days of cultivation in tanks containing 10 ppm each of As, Cd, Pb and Hg in aqueous solution, the plants were harvested and rinsed with tap water. The leaves and stems were separated and analyzed for each of the metals. The ratio of the arsenic and mercury concentrations in the leaves to the concentrations in the stems was found to be 2:1. Cadmium and lead showed a concentration ratio of about 1:1 in the leaves versus the stems. The arsenic concentration in leaves was the lowest of all the metals at 0.3 mg/g of dried plant material. The leaf concentration of cadmium was highest at 0.5 mg/g of dried plant material. Arsenic removal by water hyacinths (*E. crassipes*) was also reported by Low and Lee [360].

Phytofiltration, the use of plants to remove contaminants from water, is a promising technology [361,362]. Eapen and D'Souza [363] reviewed the use of genetic engineering to modify plants for metal uptake, transport and sequestration in order to enhance phytoremediation efficiency. Metal chelator, metallothionein (MT) and metal transporter, phytochelatin (PC) genes have been transferred to plants for improved metal uptake and sequestration. As more genes related to metal metabolism are discovered new vistas will be opened for development of efficient transgenic plants for phytoremediation.

Floating plant systems have been introduced to adsorb contaminants followed by harvesting the biomass [362]. However, these systems are not particularly efficient, especially in temperate zones [364].

The potential of using recently identified arsenic-hyperaccumulating ferns to remove arsenic from drinking water was investigated [365,366]. Hydroponically cultivated arsenic-hyperaccumulating fern species (*Pteris vittata* and *Pteris cretica* cv. Mayii) and a non-accumulating fern species (*Nephrolepis exaltata*) were suspended in water containing ⁷³As-labeled arsenic with initial arsenic concentrations ranging from 20 to 500 µg/L [365]. The arsenic phytofiltration efficiency was determined by monitoring the depletion of ⁷³As-labeled arsenic. *P. vittata* reduced the initial arsenic concentration of 200 µg/L by 98.6% to 2.8 µg/L in 24 h. An initial aqueous arsenic concentration of 20 µg/L was reduced to 7.2 µg/L in 6 h and to 0.4 µg/L in 24 h by *P. vittata*. *P. vittata* and *P. cretica* plants of same age had similar arsenic phytofiltration efficiencies, rapidly removing arsenic from water to achieve arsenic levels below the new drinking water limit of 10 µg/L. However, *N. exaltata* failed to achieve this arsenic concentration limit under the same experimental conditions. The significantly higher efficiency of arsenic phytofiltration by arsenic-hyperaccumulating fern species is associated with their ability to rapidly translocate absorbed arsenic from roots to shoots. The non-accumulating fern *N. exaltata* was unable to effect this arsenic translocation [365]. Webb et al. [367] showed that *P. vittata* L. accumulated As(III) predominantly in the leaves. The live plant maintained As as As(III), but

after biomass sample collection, aging and drying, As(III) was gradually oxidized to As(V). At very high As concentrations (ca. 1 wt.% As versus dry biomass wt.), the As was most often coordinated by sulfur and oxygen.

P. vittata (bake fern) extracts arsenic from soil and translocates it into its above ground biomass extremely efficiently [368]. Tu and Ma [369] also examined the effects pH, As and P, on the As hyperaccumulator *P. vittata* L. to optimize plant growth and maximize As removal from contaminated sites. Low pH enhanced the plant's uptake of As (pH ≤ 5.21) and P (pH ≤ 6.25). The fern had a relatively high P uptake at low pH/low As or at high pH/high As. The saddle points (turning points) were pH 6.33 and As 359 Mm for plant biomass and pH 5.87 and As 331 Mm for P uptake based on the response surface plot. Tu et al. [370] further examined the phytoremediation of arsenic-contaminated groundwater by the fern *Pteris vittata* L. Alkorta et al. [371] reviewed plants which might be used to combat arsenic poisoning epidemic.

2.2.8.5. *Human hairs*. Wasiuddin et al. [372] examined the ability of human hairs to adsorb arsenic from contaminated drinking water. Both static and dynamic tests along with the numerical modeling have been carried out to test human hairs as an adsorbent. The maximum adsorption capacity of 12.4 µg/g was reported at an arsenic concentration of 360 µg/L.

3. Some commercial adsorbents

A large number of commercial adsorbents are now available for the removal of As(III) and As(V). Representative commercially available technologies are discussed below. Since these are commercial, products the technical details are not available to the extent they would be in refereed publications.

Littleton, Colorado-based ADA technologies developed a class of amended silicate sorbents that remove more arsenic from water (<http://www.adatech.com/default.asp>) [373]. The ADA formulation was able to reduce arsenic concentration as high as 1000–10 µg/L in as little as 30 min. ADA's material removes ~2 mg/g at a concentration of 50 mg/L and about 40 mg/g at 1000 µg/L. ADA developed and commercialized an arsenic removal point of use and point of entry (POU/POE) drinking water system using Amended Silicate™ sorbents.

Aquatic Treatment Systems' (ATS) primary products (<http://www.aquatictreatment.com>) market, A/I Complex 2000, in combination with its oxidation media, A/P Complex 2002, to remove arsenic from contaminated water. The As/100 point-of-use total arsenic removal system is comprised of three cartridges connected in series. The first cartridge contains a sediment removal/activated carbon filter, which removes larger particulates such as rust and scale. The next two cartridges contain ATS proprietary arsenic removal media. Cartridge two contains oxidation media [to oxidize As(III) to As(V)]. Cartridge three contains the arsenic adsorption media. Water flows on demand from the pressure/holding tank, through an in-line activated carbon filter at a flow rate of 0.5–1.0 gal/min.

APW Inc., Reno, NV (<http://www.apwgroup.us>) developed Isorb, a ferric hydroxide-based filter media and Hedulit (Tita-

niium oxyhydrate) for the effective removal of arsenic and other contaminants from drinking water. These products are now being manufactured in Germany where they have been tested and used for years with ground and industrial waters.

Dow Chemical (<http://www.dow.com>) has developed a patent pending granular media, designed for single use operations based from technology developed at the Stevens Institute of Technology. This titanium-based product shows an improved capacity for arsenic over commercially available iron-based media. Engelhard Inc. introduced ARM 200 (<http://www.engelhard.com>), a safe, efficient and cost-effective water purification treatment for the removal of arsenic from water. Key advantages of ARM 200 include: effective removal of low levels of arsenic from drinking water. It is certified safe for drinking water use under NSF 61. Both forms of As(III) and As(V) are removed with no pre-oxidation or pretreatment required. An arsenic removal capacity >99% was found even in the presence of competing ions. ARM 200 is an adsorbent designed for use in household filters, industrial, and water utility filtration systems. An iron-impregnated ion-exchange resin was developed by Purolite (<http://www.purolite.com>) that is claimed to have equal or better capacity than competitive iron-based media. Fines are not generated and frequent backwashes are not needed. It is regenerable, disposable, and claimed to be cost effective.

EaglePicher Filtration & Minerals, Inc. (<http://www.eaglepicher.com>) developed a nanocrystalline media which removes both arsenite and arsenate without a required chemical pretreatment. The media is a ferric/lanthanum hydroxide compound deposited onto a diatomaceous earth substrate to provide a high surface area and more efficient removal. The arsenic also forms permanent bonds with the media. Removal is irreversible.

HydroFlo, Inc. (<http://www.hydroflo.com>) holds a worldwide exclusive license to remove all water-soluble forms of arsenic from water utilizing an adsorbent developed by researchers at the University of Wyoming. The technology produces no harmful by-products and removal does not require altering pH of inflow water. In addition, this method is not affected by the presence of other compounds commonly found in water, like sulfate.

In 2002, MIT, ENPHO, and RWSSSP have developed (<http://web.mit.edu/watsan/>) the KanchanTM Arsenic Filter (KAF). This is formerly called the Arsenic Biosand Filter. This filter is designed to treat arsenic and/or microbial contaminated tube well water in rural Terai in Nepal at the household level. The KAF can be constructed by trained local technicians using locally available materials such as iron nails, sand, gravel, plastic buckets, and PVC pipes. A 1-year pilot study from 2002 to 2003 showed high user acceptance and excellent technical performance.

Resin Tech (<http://www.resintech.com>) developed the TECH RESINTECH ASM-10-HP which is a strongly basic hybrid anion-exchange resin specially formulated to selectively remove arsenic. It is supplied in the salt form as clean, moist, tough, uniform, spherical beads. Company claims that RESINTECH ASM-10-HP exhibits extraordinary throughput capacity in arsenic removal service on potable water supplies. Its per-

formance is virtually unaffected by common anions, such as chlorides, bicarbonates or sulfates. It is effective over the entire pH range of potable water. RESINTECH ASM-10-HP is also available in organic trap, perchlorate-selective and nitrate-selective configured resins. These resins are fully selective for arsenic, but retain their original ion exchange selectivity.

Filtronics, Inc. (<http://www.filtronics.com>) developed Electromedia[®] IX—for fluoride and arsenic removal. It is a granulated, naturally occurring sand-like filtering media. To remove arsenic, Electromedia IX uses a fluidized bed reactor to reduce contamination to below required levels (10 ppb). Multi-Pure Drinking Water Systems (<http://www.multipureco.com>) incorporates granular ferric oxide in a carbon block cartridge. These filters are designed for POU applications. The Multi-Pure carbon filter is the first and only product to be certified by NSF International under Standard 53 for Arsenic reduction.

Isolux Technologies (<http://www.zrpure.com>) has patented IsoluxTM Technologies which effectively reduces more than 99% of total arsenic (both III and V species) without traditional pH pretreatment. ISOLUX requires no backwashing, no media handling and no hazardous waste is generated. SolmeteX scientists (<http://www.solmetex.com>) have developed and commercialized ArsenX^{np}, claimed to be a cost-effective and safe approach for the total removal of arsenic from municipal water supplies and private wells. ArsenX^{np} is a polymer-based bead product with iron oxide nanoparticles impregnated throughout the bead structure. This advanced hybrid material combines the best arsenic-binding chemistry with the robustness of water industry-standard polymer resins.

A granular iron oxide arsenic removal media (Bayoxide E33) was developed which can remove arsenic below four parts per billion (<http://www.severntrentservices.com>). This media was designed with a high capacity for arsenic and long operating cycles and low operating costs are claimed.

The three-kolshi method of removing arsenic from drinking water, which requires only clay pots, iron filings, and charcoal, is being used in Bangladesh to remove arsenic from water [374].

4. Competitive adsorption

Solute–surface interactions complicate arsenic adsorption in multicomponent systems. Solute–solute competition occurs at the active adsorption sites. Solid–liquid phase equilibrium will emerge with a different capacity for single metal ions and a new set of isotherms when competitive ions are present. The interpretation of the multicomponent systems has proved to be complex and can be a function of ionic radii, electronegativity, pH, and the availability of the active sites. Most adsorption studies were carried out using deionized water in single ion systems. Multi-ion systems have received less attention. However, environmental arsenic is always accompanied in contaminated water by other ions, so that source water's effects on the adsorbent efficiency must be explored.

Adsorption behavior of arsenic in presence of multicomponent impurities various other impurities has been studied [138,141,169,228,229,375–379]. For example, groundwater

in Bangladesh contains high concentrations of phosphates (0.2–3.0 mg P/L), silicate (6–28 mg Si/L) and bicarbonate (50–671 mg/L) [380]. More work is needed to establish mechanistic guidelines for arsenic sorption in multicomponent systems.

Competitive adsorption between As(V) and other oxyanions on kaolinite, montmorillonite, and illite and oxide minerals has been well documented [140,141]. Phosphate (PO_4^{3-}) adsorption was slightly greater at equal concentrations of PO_4^{3-} and As(V), while As(V) adsorption was greatly reduced when PO_4^{3-} was present at 10 times the As(V) concentration. Molybdate (MoO_4^{2-}) inhibited As(V) adsorption only at a pH value <4, illustrating the importance of pH and oxyanion speciation for specific adsorption.

Uptake of arsenate in the presence of phosphate at pH 4 by GFH was investigated [228]. GFH had a greater affinity for arsenate adsorption. High aqueous carbonate concentrations had little effect on As(V) adsorption onto iron oxide-coated sand at pH 7.0 in column studies of arsenic mobility and transport [375]. The adsorption of As(V) decreased marginally when the $\text{CO}_2(\text{g})$ partial pressure increased from $10^{-3.5}$ to $10^{-1.8}$ atm (a 50-fold increase in total dissolved carbonate from 0.072 to 3.58 mM). Increasing the $\text{CO}_2(\text{g})$ partial pressure to $10^{-1.0}$ atm resulted in only a slight decrease in As(V) adsorption and increase in mobility, despite a >300-fold increase in total dissolved carbonate (to 22.7 mM). When compared to phosphate, a known competitive anion, carbonate mobilized less adsorbed As(V), even when present in much higher concentrations. Carbonate did compete with As adsorption by iron oxide-coated sand. This competitive effect was relatively small versus the potential competitive effects of phosphate.

The adsorption of As(III) and As(V) onto hydrous ferric oxide (HFO in presence of sulfate and calcium ions as co-occurring solutes) was examined [229]. Decreased adsorption of both As(III) and As(V) was observed in the presence of sulfate. The effect of sulfate was greatest at lower pH. Calcium enhanced the adsorption of As(V) at high pH. This enhancement was attributed to favorable electrostatic effects arising from calcium adsorption.

NO_3^- , SO_4^{2-} , Cl^- , Br^- anions did not effect the adsorption of As(III) significantly [138]. Cl^- , and HCO_3^- interfered with arsenate removal using Bauxol by competing for surface sites [378] but Ca^{2+} did not. The suppression of arsenic sorption caused by HCO_3^- was much higher than for suppression by Cl^- [378]. The presence of Ca^{2+} , however, improved arsenic removal due to favorable electrostatic effects, as it increased the number of positively charged surface adsorption sites.

Other dissolved substances present in source water (ground or drinking) have also been reported to interfere with arsenate and arsenite mobility. The presence of natural organic matter in water may delay attainment of sorption equilibrium and suppress the extent of arsenite and arsenate adsorption. This was reported for alumina, goethite and hematite [246,381–383].

Anion competition for the available sorption sites occurs but some other factors cannot be ruled out. Other anions may slow down the time to equilibrium. Optimum times for single com-

ponent arsenate, or arsenite solutions may not be sufficient for binary or multicomponent systems [378,598].

Clearly, studies must be conducted to see the interference behavior of various ions on the adsorption of arsenic in addition to single ion adsorption systems. Multicomponent sorption models should be applied to determine the adsorption capacities [384] in multicomponent systems.

5. Comparative evaluation of sorbents

The adsorption capacities of various adsorbents tested for As(III) and As(V) removal are summarized in Table 5. It is very difficult to directly compare adsorption capacities due to a lack of consistency in the literature data. Sorption capacities were evaluated at different pHs, temperatures, As concentration ranges, adsorbent doses and As(III)/As(V) ratios. The adsorbents were used for treating ground water, drinking water, synthetic industrial wastewater, and actual wastewater, etc. The types and concentrations of interfering ions are different and seldom documented. Some adsorption capacities were reported in batch experiments and others in column modes. These cannot be compared with each other. In batch sorption experiments, the sorption capacities were computed by the Langmuir isotherm or the Freundlich isotherm or experimentally. This makes comparisons more complicated to pursue. In other words, direct comparisons of the tested adsorbents are largely impossible. Keeping these caveats in mind, some (Table 5) some adsorbents with very high capacities were chosen and compared using a 3D bar diagram (Fig. 7).

Obviously, some low-cost adsorbents developed from agricultural wastes or industrial wastes have outstanding capacities. These include treated slags, carbons developed from agricultural waste (char carbons and coconut husk carbons), biosorbents (immobilized biomass, orange juice residue), goethite, etc. (Fig. 7). Some commercial adsorbents, which include resins, gels, silica, treated silica tested for arsenic removal also performed well. Comparing sorbents by surface area alone is difficult. Adsorption of organics is usually dependent on adsorbents' surface area. The higher the surface area the greater is the adsorption. But this is often not true for metal ions/inorganics adsorption. Factors such as exchange and precipitation may contribute or dominate.

Out of the many sorbents compared in this review immobilized biomass offered outstanding performances (Fig. 7). The conditions employed in those studies can be simulated for large-scale applications for drinking water purification.

6. Arsenic desorption/sorbent regeneration

Once the sorbent becomes exhausted, the metals must be recovered and the sorbent regenerated. Desorption and sorbent regeneration is a critical consideration and contributor to process costs and metal(s) recovery in a concentrated form. A successful desorption process must restore the sorbent close to its initial properties for effective reuse. Desorption can be improved by gaining insight into the metal sorption mechanism. In most of the arsenic sorption studies discussed earlier, desorp-

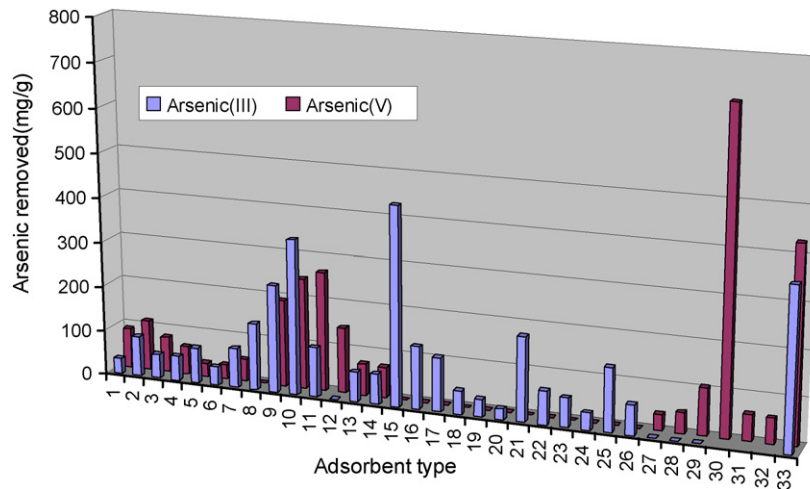


Fig. 7. Comparative evaluation among best adsorbents.

Nos.	Adsorbents	References	Nos.	Adsorbents	References
1	Char carbon	[76]	18	Co/NN-MCM-41	[301]
2	Monoclinic hydrous zirconium oxide	[315]	19	Ni/NN-MCM-41	[301]
3	Zr resin	[314]	20	Cu/NN-MCM-41	[301]
4	Iron(III)-loaded chelating resin	[305]	21	Fe/NN-MCM-48	[301]
5	Iron(III) oxide-loaded melted slag	[123]	22	Co/NN-MCM-48	[301]
6	TiO ₂	[291,292,222]	23	Ni/NN-MCM-48	[301]
7	Zirconium(IV)-loaded chelating resin	[317]	24	Cu/NN-MCM-48	[301]
8	Zirconium(IV)-loaded phosphoric chelate	[319]	25	Alkaganeite	[242]
9	Oxisol	[269]	26	Shirasu-zeolite	[182]
10	Gibbsite	[269]	27	<i>Penicillium purpurogenum</i>	[348]
11	Ferrihydrite	[235]	28	<i>Lessonia nigrescens</i>	[350,405]
12	Coconut husk carbon	[84]	29	Synthetic hydrotalcite	[275]
13	Orange juice residue	[339]	30	Immobilized biomass	[345]
14	Phosphorylated crosslinked orange waste (POW)	[340]	31	Mycan/HDTMA	[353]
15	Goethite	[237]	32	Mycan/magnafloc	[353]
16	Calcined mesoporous silica	[298]	33	Basic yttrium carbonate	[313]
17	Fe/NN-MCM-41	[301]			

tion/regeneration was not discussed. Very few desorption studies are detailed in literature. Furthermore, once arsenic is recovered in the concentrated form, the problem of how to dispose of this concentrated arsenic product must be addressed. This is a difficult task. Few attempts have been made in the literature to address the handling of concentrated arsenic wastes. Various disposal options and their advantages and disadvantages were reviewed by Leist et al. [47]. The methods frequently used for other metals and organics include combustion or recovery and purification for resale. These options are not feasible for arsenic due to the following reasons Leist et al. [47]:

1. Incineration is not practically feasible because arsenic oxides are volatile and can easily escape.
2. Recovery and purification of arsenic is not cost effective because arsenic has limited markets.

One attractive option for treating arsenic concentrates is encapsulation through solidification/stabilization followed by disposal of treated wastes in secure landfills [47,385,386]. Solidification/stabilization transforms potentially hazardous

liquid/solid wastes into less hazardous or non-hazardous solids before entombing these solids in secure landfills. This solidified/stabilized waste must satisfy leachability regulatory requirements prior to disposal [47,387–390]. According to USEPA, a waste is deemed as hazardous material if the arsenic concentration in the Toxicity Characteristic Leaching Procedure (TCLP) leachate exceeds 5 mg/L [33,155,156,269,391].

To form satisfactory storable solids, several solidification/stabilization processes have been studied. Arsenic concentrates have been incorporated into Portland cement [392,393], Portland cement and iron(II) [394], Portland cement and iron(III) [394], Portland cement and lime [395], Portland cement, iron and lime [396,397], Portland cement and fly ash [398,399], Portland cement and silicates [47,385,386,398]. The reader can find a good description of other solidification/stabilization processes in the review by Leist et al. [47]. The solidification/stabilization process has not been fully optimized. Results vary from study to study depending on the arsenic chemistry involved. Thus, it is very difficult to generalize the solidification/stabilization process. More work is needed to establish a commercial process for use on a large scale.

Few publications discuss arsenic desorption to regenerate the exhausted sorbent. Desorption has been achieved using several eluents. Sodium hydroxide [71,182,243,264,314,320,338,400] and strong acids [81,82,84,348] are most commonly used to elute both tri- and penta-valent arsenic. Selection of eluent depends on the arsenic adsorption mechanism and nature of the adsorbent. A few representatives desorption/regeneration studies are discussed below. As(V) desorption from aluminum-loaded Shirasu-zeolite was successfully achieved with 40 mM NaOH solution. This adsorbent was reused after regeneration [182]. Bead cellulose loaded with iron oxyhydroxide was regenerated when elution is carried out with 2 M NaOH solution [338]. The adsorbent was used through four cycles.

Hydrated Fe(III) oxide (HFO) dispersed on a polymeric exchanger capable of removing As(III) and As(V) was regenerated using 10% NaOH [243]. As(V) adsorbed on a Zr(VI)-loaded phosphoric acid chelating resin (RGP) was quantitatively eluted with 0.4 mol/L sodium hydroxide with regeneration of the adsorbent [320]. A large volume of aqueous 0.7 mol/L NaOH was required to elute adsorbed As(III) versus As(V). This indicated that As(III) was more strongly adsorbed by the RGP [320]. Kundu and Gupta [264] used 10% NaOH solution to desorb As(III) from iron oxide coated cement (IOCC). The adsorbent was subsequently reused for more than three cycles. Water (pH 12) was successfully used to desorb all the As(V) from mixed rare earth oxide (Raichur and Panvekar).

Attempts were made to desorb As(III) from carbon surfaces using (i) distilled water and (ii) 30% H₂O₂ in 0.5 M HNO₃ [84]. Higher desorption of As(III) by 30% H₂O₂ in 0.5 M HNO₃ is due to oxidation of As(III) to As(V), leading to the formation of neutral H₃AsO₃ and H₃AsO₄. These were not adsorbed on the positive surface of activated carbon [401,84] so they go into solution. More than 85% desorption of As(III) was achieved from exhausted fungal biomass with 0.5 M HCl confirming reversible sorption occurred [348]. The fungal biomass was recycled for 10 cycles upon desorption/regeneration. Lorenzen et al. [69] reported that As(V) desorption from activated carbon was more effective with strong acid (pH 1.5) versus a strong base (pH 12).

7. Cost evaluation

The cost of arsenic removal adsorbents developed from waste materials seldom appears in the literature. The cost of individual adsorbents depends on local availability, processing required and treatment conditions. These are not broadly and thoroughly discussed in any paper anywhere in the literature. Costs will vary when the adsorbents are made in (and for) developed countries, developing countries or underdeveloped countries. Numerous commercially available activated carbons have been used for arsenic adsorption, both as-received and after chemical modifications. However, chemical modification costs are seldom mentioned in the research reports. Furthermore, no consistency exists in the data presented. Most papers describe only batch experiments but not fixed-bed studies. Batch equilibrium adsorp-

tion isotherms cannot simulate or predict dynamic performances directly due to the following limitations:

1. Isotherms are equilibrium tests so the time restrictions are not considered.
2. Isotherms are based on carbon exhaustion-granular systems.
3. Long-term chemical and biological effects are not evident.

Most research reviewed herein has been limited to initial laboratory evaluations of solution adsorptive capacity and mechanism. Pilot-plant scale studies and cost evaluation remain to be explored. In the growing literature on natural adsorbents for arsenic uptake, little literature exists containing full costs and application comparisons of various sorbents. In addition, different sorbents are difficult to compare because of inconsistencies in the data presentation. Thus, much work is necessary to demonstrate application costs at the single home village, municipal or industrial scales.

Recently, Jessica et al. [402] investigated the cost effectiveness of selected arsenic avoidance methods. Annual costs of reverse osmosis (RO), activated alumina (AA), bottled water, and rented and purchased water coolers for various household sizes in Maine (USA) were compared. In summary, RO (\$ 411 annually) was the most cost effective, followed by AA (\$ 518) and 1-gal jugs of water (\$ 321–1285), respectively, for the households having more than one person. One-gal jugs (\$ 321) followed by 2.5-gal jugs (\$ 358) of water were the most cost effective for households of one person or for households having 0.02–0.06 mg/L As(III) and 0.08–1.0 mg/L As(V) in water. In this study, Point-of-entry systems and water coolers were not cost effective.

8. Conclusions

The heavy metals such as lead have been serious polluters of water since Roman times and perhaps earlier. They have been major water pollutants during the 20th century and continue to create serious problems in the 21st century. Mercury is a serious source of danger to top-of-the-food-chain ocean fish. As we have documented here, arsenic in drinking water is having a major human impact in several locations. Many treatment technologies are available for arsenic remediation but none of them is found to be completely applicable. Successful separation/removal processes should have:

- (a) Low-volume stream containing the concentrated contaminant(s).
- (b) A high volume exit stream containing the decontaminated liquid, solid or gas.

Adsorption is a useful tool for controlling the extent of aqueous arsenic pollution. Activated carbon was studied extensively for arsenic removal. However, carbon only removes a few milligrams of metal ions per gram of activated carbon. Regeneration problems exist. Thus, activated carbon use is expensive. Activated carbon use in developing countries is more problematic due to cost. Therefore, a definite need exists for low-cost adsor-

bents, which exhibit superior adsorption capacities and local availability.

This review shows that several materials have equal or greater adsorption capacities than activated carbon. Many candidates appear interesting, exhibiting both advantages and disadvantages. Activated alumina is very efficient and can be regenerated *in situ* to extend the useful life. However, sorption efficiency is highest only at low pH and arsenites must be pre-oxidized to arsenates before adsorption. The removal efficiency of ion-exchange resins is independent of water pH and the adsorbent and can be also be regenerated *in situ*. However, sulfates, nitrates or dissolved solids reduce adsorption efficiency. Therefore, additional/preventive steps must be applied to utilize these exchangers for arsenic adsorption. Clays, silica, sand, etc. are in fact low-cost adsorbents (and substrates). They are available worldwide. These can also be regenerated *in situ*. Unfortunately, they have lower adsorption efficiency than most of the other adsorbents. Additionally, other water contaminants can deactivate the clays, further lowering the sorption efficiency. Organic polymers are also good adsorbents with *in situ* regenerable capability. Cost makes them less attractive and other contaminants such as dissolved solids present in water reduce their sorption efficiencies. Dried roots of the water hyacinth and some other plants could also be used to reduce arsenic concentrations in water. This technology needs to be properly optimized.

Iron or iron compounds [iron oxides, oxyhydroxides and hydroxides, including amorphous hydrous ferric oxide (FeO-OH), goethite (α -FeO-OH) and hematite (α -Fe₂O₃), etc.] are the most widely used adsorbents, having higher removal efficiency at lower cost versus many other adsorbents. Additionally, they oxidize arsenites to arsenates. They represent the majority of commercial systems. However, their adsorption efficiency is highest only at low pH and they are not regenerable. Still iron-based sorbents (IBS) constitute an emerging treatment technology for arsenic removal. IBS have a strong affinity for arsenic under natural pH conditions, relative to activated alumina and other adsorbents. This feature allows IBS to treat much higher bed volumes without the need for pH adjustment, unless the pH is >8. Despite the dominance of iron compounds, other opportunities exist.

Solid wastes are a vexing societal problem mandating attention to recycling. Recycled product quality is not always high or recycle may not be feasible. However, conversion of solid wastes into effective low-cost adsorbents for wastewater treatments could decrease costs for removing arsenic. A perusal of Table 5 illustrates that many activated carbons, from wastes, have high adsorption capacities and can also be regenerated, further reducing treatment costs. Clay minerals, fly ash, fertilizer wastes, different types of coal, slags, zeolites, etc. can serve as arsenic scavengers. Only initial laboratory evaluations of the adsorptive capacities of adsorbents developed from such wastes were available at the time this review was written. Future scale-up studies are called for with careful cost evaluations.

Most adsorption media (or adsorbents) preferentially adsorb charged species. Most inorganic contaminants dissociate to some degree in water depending upon pH. Therefore, these contaminants exist as a charged species somewhere throughout the

pH range. As(V), for example, exists as a charged species in water across a wide range of pH. However, As(III) exists as a charged species across a much narrower range of pH. As(III) is uncharged in the relatively neutral pH range of most groundwater, explaining why As(V) is better adsorbed on most media than As(III).

The active sites on the adsorption media may also exhibit charge over certain pH ranges, therefore a basic understanding of both the target contaminant's charge behavior and that of the adsorbent are useful in determining if pH adjustment would be beneficial or necessary in a particular treatment application. The removal of arsenic by most of the adsorbents increases somewhat as pH is reduced. Some adsorbents become unstable outside of a certain pH range. Activated alumina actually deteriorates at high pH. Most of the commercially available adsorbents are designed for application only within specific pH ranges.

Selection of a suitable sorbent media to supply arsenic free drinking water depends on (1) the range of initial arsenic concentrations, (2) other elements and their concentration in water, (3) optimization of adsorbent dose, (4) filtration of treated water, (5) adjustment of pH in water, (6) post treatment difficulties, (7) handling of waste and (8) proper operation and maintenance. The adsorbents' active sites may be occupied by other contaminants based on its selectivity, thereby reducing the effective adsorption capacity for the target contaminant. Understanding the sorbent's selectivity sequence and knowing the water quality profile will help avoid competitive adsorption.

Adsorbent selection is a complex decision. The choice changes depending on the oxidation state of arsenic and the many other factors discussed above. Sorbent technologies, which are successful in the laboratory, may fail in field conditions. Thus, the selection of the appropriate technology/sorbent media can be tedious. The Best Available Technology (BAT) method can assist sorbent selection. The BAT can be defined as: the best technology treatment techniques which are available after examination for efficacy under field conditions (taking cost into consideration). For the purposes of setting MCLs for synthetic organic chemicals, any BAT must be at least as effective as granular activated carbon (<http://www.nsc.org/ehc/glossary.htm>) or the best economically achievable technology that reduces negative impacts on the environment (<http://www.abag.ca.gov/bayarea/sfep/reports/ccmp/ccmpappb.html>). Alternatively, the most effective, economically achievable, and state-of-the-art technology currently in use for controlling pollution, as determined by the US EPA (http://www.great-lakes.net/humanhealth/about/words_b.html) can be used for comparison.

The BAT can be designated based upon criteria, including high removal efficiency, affordability (using large system as the basis), general geographic applicability, and compatibility with other water treatment processes, process transferability, and process reliability. If the process has to be developed for underdeveloped countries, like Bangladesh, than it should be simple, low-cost, based on local resources and skills. The process should function without electricity and widely accessible to community.

Adsorption is but one tool in effort to remove arsenic from drinking water. Currently, about 100 million people are consuming water with arsenic concentration up to 100 times the 10 $\mu\text{g/L}$ guideline of the World Health Organization [24,403]. A recent article in Science [404] focusing on the drinking water problems in Bangladesh demonstrated that two different approaches have had maximum impact: (1) testing tube wells followed by switching away from contaminated wells to alternate uncontaminated water sources and (2) installation of deep wells that supply water from older aquifers that do not contain elevated arsenic levels. Furthermore, three major recommendations were made: (a) stimulate the periodic monitoring of water quality no matter what mitigation option exist, (b) encourage the wise use of deep aquifers low in arsenic, and (c) publicize widely the known effects of arsenic on the mental development of children. This common-sense approach illustrate that a variety of low-cost approaches must be employed in many underdeveloped locations throughout the world. Only when these approaches are exhausted will adsorption be likely to contribute to further mitigation efforts.

This review (and Table 5) should help in initially screening various sorbent media for setting up the treatment plants based on the community level or household levels in developed, developing and underdeveloped countries. For further adsorption/arsenic removal methods reading, see the literature cited in refs. [601–616].

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