

1 **Selective removal of arsenic in water: A critical review**

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25 **Abstract**

26 Selective removal of arsenic (As) is the key challenge as this not only increases the efficiency
27 of removal of the main As species (neutral As(III) and As(V) hydroxyl-anions) but also allows
28 the reduction of waste significantly as it does not co-remove other solutes. It increase the
29 capacity and lifetime of units, while lowering the cost of the process. A sustainable selective
30 mitigation method should be considered in relation to the economic resources available, the
31 ability of infrastructure to sustain water treatment and the options for reuse and/or safe disposal
32 of treatment residuals. Several methods of selective As removal have been developed, such as
33 precipitation, adsorption and modified iron and ligand exchange. There are two types of
34 mechanisms involved with As removal: Coulombic or ion exchange; and Lewis acid-base
35 interaction. Solution pH is one of the major controlling factors limiting removal efficiency
36 since most of the above-mentioned methods depend on complexation through electrostatic
37 effects. The different features of two different As species make the selective removal process
38 more difficult, especially under natural conditions. Most of the selective As removal methods
39 involve hydrated Fe(III) oxides through Lewis acid-base interaction. Microbiological methods
40 have been studied recently for selective removal of As although there have been only a small
41 number of studies; however, the method shows remarkable results and indicates positive
42 prospects for the future. The biggest challenges in selective removal of As is the presence of
43 phosphate in water which is chemically comparable with As(V).

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45 ***Keywords:* Selective Arsenic removal from water; Competitive ions impacting removal;**

46 **Waste reduction; Cost reduction**

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51 **1. Introduction**

52 Arsenic (As) is a metalloid and a human carcinogenic substance that can be found in
53 both organic and inorganic forms. Elemental As is a crystalline solid with silver-gray
54 appearance. The atomic weight of As is 74.9 amu (atomic mass unit) and the melting and
55 boiling point is 817 and 613 °C, respectively. Its vapor pressure is 1 mm Hg at 372 °C. Arsenic
56 is an element that is commonly distributed in the atmosphere, rocks, minerals, soil, water and
57 in the biosphere (Basu et al., 2014). In the earth's crust, seawater and the human body, it is the
58 20th, 14th and 12th most common element, respectively (Baig et al., 2015; Matschullat, 2000;
59 Mohan and Pittman Jr, 2007).

60

61 More than four thousand freshwater systems found globally, require As mitigation
62 measures to meet the guidelines of the World Health Organization (WHO) for drinking water
63 supply (WHO, 2011). The majority of these systems are groundwater reservoirs (DeMarco et
64 al., 2003). Natural contamination through As mobilization from geogenic sources is the major
65 reason for the presence of As (up to >1000 µg/L) in most groundwater resources (Vatutsina et
66 al., 2007). Human activities such as mining and related processes can accelerate this release of
67 As by several orders of magnitude. With the increasing global population, the agricultural
68 demand and excessive groundwater withdrawal have resulted in the dissolution of As within
69 the aquifers (Sarkar et al., 2012). In addition, there are anthropogenic sources of arsenic
70 affecting water resources and other environments such as poultry and swine feed additives,
71 pesticides (monosodium methyl arsenate (NaMeHAsO₃), disodium salt (Na₂MeAsO₂)),
72 herbicides, wood treatment agents (chromate copper arsenate), electronic manufacturing, cattle
73 dips, vitamin supplements, pharmaceuticals, nutraceuticals, coal combustion, cigarettes, paints,
74 dyes, cosmetics and highly soluble trioxide stockpiles (Basu et al., 2014; Kumar et al., 2019).

75 More than 60% of anthropogenic As globally emitted originates from coal combustion and Cu
76 smelting processes (Baig et al., 2015; Mohan and Pittman Jr, 2007; Smedley and Kinniburgh,
77 2002). With such natural and anthropogenic factors, there are more than 105 countries and over
78 202 million people which globally suffer from As contamination. Some of the most affected
79 countries are Bangladesh, Vietnam, USA, West Bengal (India), Taiwan, Cambodia, Canada,
80 Germany, Hungary, Japan, Laos, Nepal, Pakistan, Poland, Romania, Thailand, UK, Ghana,
81 China and Latin American countries including Mexico, Argentina, Chile and Nicaragua (Asere
82 et al., 2019; Bundschuh et al., 2010; Hlavay and Polyák, 2005; Litter et al., 2010; Luong et al.,
83 2018; Shakoor et al., 2017; Shakoor et al., 2016; Singh et al., 2015). In water, 95% of the As
84 occurs in inorganic forms (Maity et al., 2019; Shinde et al., 2013). Generally, the inorganic
85 forms of As are found in several oxidation forms such as -3, 0, +3 and +5 (not all are found in
86 the natural condition). In natural systems, they are mostly present as As(III) or As(V); thereby
87 speciation depends on solution pH and the redox potential (Eh) values (Kumar et al., 2019;
88 Vatutsina et al., 2007). In groundwater, the oxidation status of the inorganic As is decided by
89 water chemistry and exposure to the air (Xu et al., 2013). The toxicity of most organic As
90 species is lower than that of inorganic As species with As(III) being more toxic than As(V)
91 (Cullen and Reimer, 1989; Jain and Ali, 2000; Shinde et al., 2013). As(V) is generally
92 considered as a soft acid and it is available as AsO_4^{3-} , HAsO_4^{2-} , and H_2AsO_4^- species while
93 As(III) presents as AsO_3^{3-} , $\text{AsO}_2\text{OH}^{2-}$, $\text{As}(\text{OH})_4^-$ and $\text{As}(\text{OH})_3$, which are considered to be hard
94 acids (Baig et al., 2015; Greenwood and Earnshaw, 2012). Both As(III) and As(V) species are
95 subjected to chemically and microbially mediated redox and methylation reactions in water
96 (Andreae and Klumpp, 1979; Freeman et al., 1986; Hlavay and Polyák, 2005). However, in
97 groundwater, both As(III) and As(V) species can coexist, as redox reactions for conversion in
98 between both species are slow (Litter et al., 2010; Vatutsina et al., 2007). Under natural
99 conditions, the As(V) (hydroxy anions) and As(III) (neutral species) species show remarkable

100 differences because of their electronic structure, polarizability, dissociation behavior, sorption
101 affinity and toxic nature (Cullen and Reimer, 1989; Jain and Ali, 2000; Shinde et al., 2013).
102 Therefore, the removal of these As species requires different measures in most of the removal
103 processes (Vatutsina et al., 2007).

104

105 The toxicity of As has been widely discussed and reported in the literature (Baig et al.,
106 2015; Choong et al., 2007; Jain and Ali, 2000; Kavcar et al., 2009). Arsenic exposure has been
107 linked to a number of cancerous and non-cancerous impacts in both acute and, non-acute forms
108 (An et al., 2005; Awual et al., 2019; Mohan and Pittman Jr, 2007). In carcinogenic grouping,
109 As has been categorized into group 1 elements (Nurchi et al., 2020). Hence, As is one of the
110 major elements producing cancer (Baig et al., 2015; Cutter, 1992; Litter et al., 2010). A
111 concentration of 3 µg/L of As in drinking water creates the risk of bladder and lung cancer (4-
112 7 deaths/10,000 people) (An et al., 2005). Moreover, As is a teratogen which can pass cross
113 the placental membrane into the metabolic system of the unborn child. Further, it is also a
114 cumulative substance passing out of the body through hair, fingers, urine, nails and skin, which
115 makes hair, urine and nails ideal biomarkers for As exposure (Basu et al., 2014; Dissanayake
116 and Chandrajith, 2009). Ischemic heart disease (Basu et al., 2014; Hsueh et al., 1998; Tseng et
117 al., 2003), Blackfoot disease (Basu et al., 2014; Huang et al., 2003; Tseng, 2008; Tseng et al.,
118 1996), cardiovascular diseases (Basu et al., 2014; Wang et al., 2007), Chronic Kidney Disease
119 (CKDu) (Basu et al., 2014; Hsueh et al., 2009), Bowen's disease (Basu et al., 2014; Çöl et al.,
120 1999; Salazar et al., 2004), Alzheimer's disease (Basu et al., 2014; Çöl et al., 1999; Dani, 2010;
121 Salazar et al., 2004) are some other health problems due to As consumption. Considering the
122 global emerging danger through As exposure, the World Health Organization (WHO) has
123 lowered the As guideline value for drinking water from 50 to 10 µg/L (Litter et al., 2010; WHO,
124 2011).

125

126 One of the challenges in many water and wastewater treatment plants worldwide is the
127 selective removal of trace elements such as As with the presence of higher concentrations of
128 background competing solutes such as main ions (Mandal et al., 2013; Ramana and Sengupta,
129 1992). Most of the conventional As removal methods that will be discussed in section 2
130 generally pose higher removal efficiencies, but lack the ability to compete with background
131 ions and are not cost-effective (Korngold et al., 2001; Pincus et al., 2019). Therefore, the
132 conventional methods are jeopardized in practical applications due to economic, environmental
133 or social aspects and, it creates several gaps for selective As removal. This challenge becomes
134 even bigger as most of the As contaminated water systems are contaminated only with As, the
135 fraction of which is very small compared to other dissolved chemical compounds that in
136 addition are often essential in drinking water. Otherwise, water is often suitable for
137 consumption. In this case, the As removal mechanism should eliminate only As to gain an
138 efficient application approach and selective removal is, therefore, is a key goal. Moreover, the
139 behavior of As in water is disturbing to the removal efficiency of As, as it generally decreases
140 with increased initial As concentration. Therefore, the selective removal method should ensure
141 a strong affinity with As despite its initial concentration. Moreover, it is a well-known fact that
142 most of As removal methods require pre-oxidation and post-treatment steps to make sure the
143 removal of As(III). Therefore, it is a key goal to finds and selects a method that does not require
144 pre- and post-treatment to reduce the energy requirement and the complexity and cost of the
145 process. The next key goal with any of the As removal methods is the reduction of waste
146 production. In any of the non-selective treatments, large amounts of other solutes (in particular
147 ions) are removed, and the resulting waste management is high in cost for both the environment
148 and the economy and therefore, reduction of volumes of As-rich waste is a key goal of a
149 selective As removal process as it can reduce the amount of waste by several orders of

150 magnitude. Moreover, as two principal As species, i.e. As(V) and As(III) act differently,
151 selective removal is more difficult in natural conditions.

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154 **2. Overview of common arsenic removal methods**

155 The As remediation can be categorized into major 4 groups: ion-exchange processes,
156 membrane separation processes, precipitative processes, and adsorptive processes which
157 generally include pre-oxidation in case of As(III) removal needs (Abejón et al., 2015; Baskan
158 and Pala, 2010; Bundschuh et al., 2011; Jadhav et al., 2018; Yüksel et al., 2018). Figure 1
159 represents different methods within the above four remediation methods. Coagulation using
160 ferric chloride followed by microfiltration removes As(III) (after pre-oxidation) and As(V)
161 equally but the method is not suitable for water that has trace amounts of As and it will produce
162 a high amount of As-containing sludge (Kobyta et al., 2020; Sarkar et al., 2012). In ion-
163 exchange processes, the conventional ion-exchange methods always reduce the As removal
164 capacity with the competition of other anions in water. Adsorptive measures have received
165 positive attention due to their easy use and low cost (not common for all adsorbents), compared
166 to most of the other remediation methods. Considering the environmental cost of most of the
167 conventional methods there is significant research interest in natural-based adsorbents in order
168 to remove As in water. With well-designed chemical modifications, the As removal was
169 successful with these natural-based adsorbents (Asere et al., 2019; Kumar et al., 2019). Soil
170 minerals such as iron coated pottery granules (Baig et al., 2015; Dong et al., 2009),
171 impregnated-tablet ceramic adsorbents (Baig et al., 2015; Chen et al., 2012), agricultural waste
172 materials such as rice polish (Baig et al., 2015; Ranjan et al., 2009) and impregnated-activated
173 rice husk carbon (Baig et al., 2015; Mondal et al., 2007), industrial waste materials such as
174 granulated slug (Ahn et al., 2003; Baig et al., 2015; Zhang and Itoh, 2005) and fly ash (Baig et

175 al., 2015; Diamadopoulos et al., 1993), plant biomass such as biochars from plant materials
176 (Allen and Brown, 1995; Allen et al., 1997; Baig et al., 2015; Mohan and Chander, 2006),
177 aquatic biomass such as chitosan (Baig et al., 2015; Gupta et al., 2009), activated carbon
178 materials such as Fe³⁺ impregnated granular activated carbon (Baig et al., 2015; Mondal et al.,
179 2007), calcium impregnated granular activated carbon (Baig et al., 2015), metal-loaded coral
180 limestone (Maeda et al., 1992; Xu et al., 2002), hematite feldspar (Singh et al., 1996; Xu et al.,
181 2002), sandy soils (Kuhlmeier, 1997; Xu et al., 2002), lanthanum loaded silica gel (Xu et al.,
182 2002), activated alumina (DeMarco et al., 2003; Kim et al., 2004), and activated mud (Genç-
183 Fuhrman et al., 2004) are some of the adsorptive materials that have been used for As removal
184 in water.

185

186 Generally, the electronic structure of As (especially of arsenate (As(V))) is very similar
187 to phosphorus/phosphate and so the chemistry of As is comparable with that of phosphorus
188 (Bui et al., 2019). Therefore, the removal of As interferes with the presence of phosphate or
189 phosphorus compounds (Basu et al., 2014). Other than phosphorus, the presence of silicate,
190 sulfate, chloride and bicarbonate are some of the ions that can interfere with As removal and
191 will also be removed, together with As increasing waste product and cost while reducing the
192 lifetime of the removal unit (Basu et al., 2014; Gu et al., 2005).

193

194 Most of the conventional or modified conventional As treatment methods require
195 further removal techniques such as micro-filtration, to meet the guidelines, creating less cost-
196 effectiveness in the whole process (An et al., 2005). The commercially available resins as ion-
197 exchangers are economically less competitive for As removal as they have a lack of selectivity
198 toward As. The polymeric anion exchangers would not be suitable for selective removal of As,
199 as such exchangers are selective on sulfate ions over As (DeMarco et al., 2003). Therefore,

200 there is a growing demand for economically and environmentally feasible novel materials for
201 selective removal of both (As(III)) and As(V) with a similar high affinity for both of them
202 (Gupta et al., 2012).

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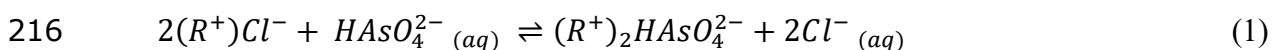
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205 **3. Common mechanisms for arsenic removal in water**

206 With either selective or non-selective As removal, the mechanisms involved are
207 common for most of the time, despite the different types of equipment and protocols used.
208 There are two types of mechanisms involved with As removal; Coulombic or ion exchange and
209 Lewis acid-base interaction (Sarkar et al., 2012).

210 The As(V) oxyanions pose negative charges and therefore the ion-exchange mechanism is most
211 suitable for removal of As(V) especially in most of the conventional ion exchange processes.
212 over a broad range of pH, where As(V) exists as an oxyanion. For example, if the solution is
213 at above neutral levels As(V) is found as a divalent anion and can be removed using an anion
214 exchanger in chloride form (Eq. 1)

215



217

218 where R^+ represents the anion exchanger with fixed positive charges. As stated in the
219 introduction section the groundwater always consists of other innocuous anions such as
220 chloride, bicarbonate, sulfate as well as phosphate simultaneously with As. The As removal
221 efficiencies in ion exchangers are greatly impacted by the above common anions and they
222 always play a role in reducing the As(V) uptake and chromatographic elution of As(V).
223 Therefore, unless there is a specifically modified selectivity in ion exchangers toward As, the
224 conventional ion exchange methods will not effectively remove As in water. As(III) which

225 occurs in non-ionic form cannot be removed through ion-exchange methods unless there is a
226 pre-treatment process to convert As(III) into As(V) (Sarkar et al., 2012).

227

228 The second possible mechanism for As removal is Lewis acid-base interaction. Both
229 As(III) and As(V) are strong ligands or Lewis bases as they can donate lone pairs of electrons.
230 H_2AsO_4^- and HAsO_2 are monodentate ligands which have one donor atom per molecule, while
231 HAsO_4^{2-} is a bidentate ligand with two donor oxygen atoms. Thus, As(III) and As(V) show
232 high sorption affinity towards solid surfaces with Lewis acid characteristics. Sulfate, chloride
233 and bicarbonate ions are poor ligands compared to both As(III) and As(V). Therefore, if there
234 is a Lewis acid surface to catch the As(III) and As(V), there will be selectivity behavior and
235 high affinity towards As(III) and As(V). In literature, there have been several attempts made
236 to remove As(III) and/or As(V) using the Lewis acid-base interaction (An et al., 2005; Awual
237 et al., 2019; Shinde et al., 2013; Singh et al., 2018). Metal ions such as Cu(II), Fe(III) (An et
238 al., 2005), Zr(IV) (Awual et al., 2019) and thiol groups (Singh et al., 2018) have been used as
239 Lewis acid for removal of As(III) and As(V), and this will be further discussed in section 5.

240

241

242 4. Selective removal of arsenic in water

243 In natural water systems, cations and anions have a high affinity for interacting with
244 hydrous oxide surfaces. Therefore, metals and metalloids like As can be removed with the use
245 of oxide and hydroxide surfaces. Iron oxide/hydroxide is one of the most used ingredients in
246 terms of selective removal of heavy metals and metalloids, including As in water (Hao et al.,
247 2018). Iron-based oxides/hydroxides have several advantages, including high affinity towards
248 As species and have easy access as they are abundant on earth and are environmentally friendly

249 in their use (Hao et al., 2018). Table 1 briefly depicts selective adsorbents of As and their
250 behavior in selective As removal in aqueous media.

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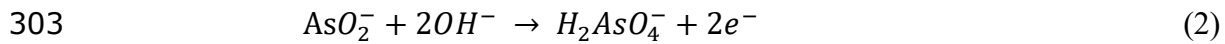
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253 **4.1. Selective removal of arsenic by the electrocoagulation method**

254 The electrocoagulation method for selective arsenic removal has been identified as one
255 of the most simple and efficient methods in use (Ali et al., 2013). In electrocoagulation, the
256 basic mechanism for removal of As(III) from water involved two steps: (1) conversion of
257 As(III) into As(V) (Eq. 2). Due to the conversion of As(III) into As(V), the presence of As(III)
258 usually slows the removal process (Kumar et al., 2004; Wan et al., 2011). The second step is
259 removal of As(V) via generation of coagulants due to oxidation of the sacrificial anode. The
260 latter step consisted of three sub-steps. First, with the voltage, the sacrificial anode goes through
261 an oxidation process and produce a coagulant which is insoluble in water. Several anodes that
262 used in electrocoagulation (in As removal) are Zn, Fe and Cu (Ali et al., 2013; Ali et al., 2012;
263 Wan et al., 2011). The Zn and Cu anodes generate $Zn(OH)_2$ and $Cu(OH)_2$ coagulants
264 respectively. As the second sub-step, the As(V) adsorbs into the surface of the coagulant and
265 further, As(V) replaces the hydroxyl groups of the developed coagulant making complexes
266 such as $ZnHAsO_4$ and $CuHAsO_4$. Finally, the flocs settle and the sedimentation and filtration
267 steps also should be employed to complete the removal process. The presence of competing
268 ions such as sodium, potassium, magnesium, calcium, sulphate, nitrate and chloride do not have
269 negative impact on removal of As(III) and As(V). The dissolved anions are provide
270 advantageous conditions in electrocoagulation method as the anions provide conductivity to
271 the solution. The As removal is increasing with the conductivity and after specific value the
272 adsorption become constant at the highest adsorption level (Ali et al., 2012). This specific
273 conductivity level is nearly similar to the conductivity of natural water (1.43 mS/cm).

274 Regarding sodium chloride it require 200 mg/L of sodium chloride to get the above mentioned
275 conductivity level (Ali et al., 2012). Therefore, the more anion in water make higher
276 As(III)/As(V) removal in electrocoagulation but no inhibition activities. Sometimes, the
277 presence of different competitive ions will not directly interact with As adsorption but may
278 inhibit the adsorption/removal indirectly. For example, with Fe anode, presence of silica will
279 be inhibit or lower the production of coagulant that responsible for adsorption of As(V) in the
280 solution (Wan et al., 2011). Therefore, the type of ions presence will be decided the most
281 suitable electrodes. However, the electrocoagulation method does not always act in a selective
282 manner for As(III) and/or As(V) removal in water if phosphate is presence. It can prove with
283 the literature, the Zn-Zn and Cu-Cu electrodes can successfully remove the As(III) and As(V)
284 without any interference of phosphate (Ali et al., 2013) but Wan et al. (2011) showed the
285 electrocoagulation of As(III) and As(V) with Fe electrode inhibited by 1 and 4 mg/L of
286 phosphate respectively, due to similar chemistry of phosphorous with As. By using long
287 operational times and electrode that produce sufficient amount of iron oxide, it removed both
288 As and phosphate but not selectively As. After As(III) removal by electrocoagulation, the
289 resultant water have similar conditions for all of the other parameters such as ion
290 concentrations, temporary and permanent hardness, alkalinity, total dissolved solids (TDS) (Ali
291 et al., 2013; Ali et al., 2012). The pH can be slightly increased in treated water within the
292 accepted range for water quality guidelines. It has been reported that the maximum percentage
293 of As(III) removal can be achieved as high as 99.5% under the electrocoagulation method (Ali
294 et al., 2013; Ali et al., 2012). The electrocoagulation removes phosphate simultaneously with
295 As due to the same chemistry of both of them (Wan et al., 2011). Therefore, the
296 electrocoagulation does not successful enough if there are phosphate in the water. In
297 electrocoagulation, the pH is an important factor to determine the As removal amount. The
298 maximum As(V) removal percentage can achieve at the pH 7 and moreover at pH 7 the removal

299 is quick. When the pH is lower than 7 it may remove significant amount of As (similar as at
300 pH 7) but takes longer time. The higher pH than 7 require longer time to remove As but not
301 same as at pH 7. The fact make easier the removal process since the natural water is at the pH
302 levels of around 7. (Ali et al., 2013; Kumar et al., 2004; Wan et al., 2011).



304

305 The electrocoagulation method can be used for selective removal of both As(III) and
306 As(V) when correct electrodes are used; however, there are still, some significant
307 disadvantages found. The production of a large amount of coagulant, rich with As will require
308 additional measures for safe disposal. The additional energy must be employed to filter the
309 coagulant in order to receive clean water. Therefore, electrocoagulation is an energy-
310 consuming method when compared to most of the other available selective As removal
311 methods.

312

313

314 **4.2. Selective arsenic removal by adsorption**

315 Adsorption is one of the most employed methods in selective As removal studies. Fe
316 based methods are common in selective As removal through adsorption. The basic
317 phenomenon of Fe based adsorption methods is discussed in section 5.2. However, all the
318 adsorptive materials are different. Hlavay and Polyák (2005) have prepared a novel adsorption
319 material for As(III) and As(V) removal in water by in situ precipitation of Fe(OH)₃ on the
320 surface of granulated activated Al₂O₃ as supporting material (surface of activated Al₂O₃
321 covered with Fe(OH)₃). It has been identified and classified by USEPA that activated alumina
322 is one of the best available technologies for As removal in drinking water (Weidner and
323 Ciesielczyk, 2019) due to its relatively high surface area. Moreover, activated alumina has a

324 selectivity towards As(III) and As(V) (Clifford, 1999; Weidner and Ciesielczyk, 2019). One of
325 the key advantages of this novel adsorbent is its mechanical and chemical stability in aqueous
326 environments. The key adsorption mechanism of Fe(OH)₃ precipitated on Al₂O₃ material is
327 chemisorption. The As(V) forms inner-sphere complexes with both Al and Fe oxide (Figure
328 2). Meanwhile, As(III) forms both inner-sphere and outer-sphere surface complexes on Fe
329 oxide and outer-sphere surface complexes on Al oxide (Goldberg and Johnston, 2001; Hlavay
330 and Polyák, 2005) (Figure 2). This particular adsorbent can be used as a selective sorbent for
331 removal of As from aqueous solutions according to the authors, but no data have been reported
332 for absorbance of As in the presence of interactive ions. However, there is evidence that
333 precipitated Fe(III) oxides are selective for As species in aqueous solutions (DeMarco et al.,
334 2003; Vatutsina et al., 2007). Xu et al. (2002) have developed a new adsorbent, aluminium-
335 loaded Shirasu-zeolite P₁ by treating a P₁ type Shirasu-zeolite (of volcanic origin) with
336 aluminium sulfate solution. The adsorption of As(V) has occurred through chemisorption with
337 active sites of aluminium species which is mostly aluminium hydroxide that is loaded in
338 Shirasu-zeolite P₁. The adsorption of As into aluminium-loaded Shirasu-zeolite, P₁ depends on
339 the pH of the containing solution and the effective pH range is pH 4-10. The adsorption
340 capacity was 0.1 mmol/g (initial solution 1.3 mM/20 mL) obeying the Freundlich isotherm
341 equation. The study suggests that this particular sorbent is suitable even for low As(V)
342 concentration ranges (<200 µg/L). There is no significant interference of As(V) adsorption with
343 As(III), chloride, nitrate, sulfate, chromate and acetate ions in the solution. However,
344 significant suppression of As(V) adsorption occurred with the presence of phosphate ions in
345 the solution as phosphorus competes with As for adsorption sites (Xu et al., 2002).

346

347 Chromium-based metal-organic framework hosted Fe₃O₄ nanoparticle (MIL-101-Cr-
348 Fe₃O₄) also can be identified as Fe based adsorptive material with modifications (Folens et al.,

2016). The chromium-based metal-organic framework hosted Fe₃O₄ nanoparticle (MIL-101-Cr-Fe₃O₄) shows a high affinity towards both As(III) and As(V) in water. The adsorption capacities are 121.5 and 80.0 mg/g, respectively. The results show that the integration of encapsulated Fe₃O₄ nanoparticles and the chromium-based metal-organic framework have enhanced the adsorption capabilities more significantly than using them alone. The encapsulated Fe₃O₄ nanoparticles could remove 75.5 and 37.4% of As(III) and As(V) whereas the chromium-based metal-organic framework could remove 22.8 and 92.4%, respectively. The integration showed 94.7 and 99.9% removal, respectively. The encapsulated Fe₃O₄ nanoparticles have less selectivity towards As(V) and at the aqueous media the nanoparticles are subjected to aggregation and therefore, even for the As(III), the sorption capacities are low. On the other hand, the chromium-based metal-organic framework has less selectivity towards As(III) but the integration could increase the selectivity for both As(III) and As(V) while avoiding the aggregation of the nanoparticles (Folens et al., 2016). Most importantly, the presence of Ca²⁺, Mg²⁺ and phosphate has not created any impact on As(III) and As(V) adsorption. The MIL-101-Cr host material consisted of two types of mesoporous cages with 29 and 34 Å; therefore, the particular host material is very attractive to high loadings of Fe nanoparticles which leads to high As(III) and As(V) adsorption capacity. The best pH range for the particular adsorptive material is 7-10. In literature, there are several studies based on metal-organic frameworks. Some of the other metal-organic frameworks that have been used to remove As(III) or As(V) are ZIF-8 nanoparticles (Jian et al., 2015), ZIF-8(Zn) (Wu et al., 2014), Fe-BTC (Zhu et al., 2012) Of them, ZIF-8 nanoparticles are effective for use with low As(III) and As(V) concentrations. The study has been conducted with 100 µg/L of total As solution and with 0.06 g/L of ZIF-8 nanoparticles of As(V) concentration in the water sample has been decreased dramatically to 2.8 µg/L. However, the As(III) only decreased to 73 µg/L even with a high ZIF-8 dosage of 0.2 g/L (Jian et al., 2015). In aqueous media, the ZIF-8

374 adsorbs the water molecules and generates activated sites such as zinc hydroxyl, secondary
375 amine and tertiary amine via a protonation reaction. Those positive sites adsorb the negative
376 As(V) species efficiently via electrostatic attraction. The presence of sulfate and nitrate as
377 competitive anions in the solution has no impact on As(III) and As(V) sorption even when the
378 concentration of the above anions is 100 times higher than the As(III) or As(V) concentration.
379 However, phosphate and carbonate ions will significantly decrease As(III) and As(IV)
380 adsorption. The phosphate has a similar chemistry as As and therefore, it competes with all the
381 adsorption sites while the carbonate ions compete for zinc hydroxyl sites (Jian et al., 2015).
382 These results are similar to those of Folens et al. (2016) which also have a metal-organic
383 framework. Folens et al. (2016) showed that a pure organic metal framework (without
384 modification) has a higher affinity towards As(V) than As(III) and the same fact has been
385 proved with some of the other organic metal frameworks in As(III) and As(V) adsorption (Jun
386 et al., 2015)

387

388 The Technical University of Berlin in Germany has developed an As removal technique
389 with granular ferric hydroxide in fixed bed reactors (Driehaus et al., 1998). The reactors were
390 effective at As removal and no interference of other anions except phosphate occurred.
391 Although phosphate adsorption is lower than As adsorption, phosphate concentration
392 exceeding those of As could suppress the As adsorption significantly. One of the disadvantages
393 of the use of granular ferric hydroxide on As removal is that as time passes, the capacity of
394 removal decreases (freshly prepared granular ferric hydroxide are better at As removal than old
395 ones). The adsorption capacity decreases with an increasing solution pH (for detailed results
396 see Driehaus et al. (1998) and Vatutsina et al. (2007)). As mentioned earlier, the granular
397 particles can end up in the effluent (Driehaus et al., 1998). This particular adsorbent is most

398 suitable for small water suppliers due to operational needs, pH adjustments, and less capability
399 in reuse as well as requiring doses of chemicals.

400

401 Another adsorbent, hydrous Fe(III) bound with polyacrylamide made by Shigetomi et
402 al. (1980), selectively removed As(V) from aqueous solution. The optimum adsorption was
403 achieved in the range of pH 5-8. The arsenate adsorption capacity was 43 mg/g of the adsorbent.
404 Regeneration of adsorbent with 0.01 mol/L HCl acid restored the initial adsorbent capacity.

405

406 Apyron Technology, Inc. has developed a large-scale As removal system using
407 inorganic granular activated alumina metal oxide (Ahmed, 2001). This particular system is a
408 point-of-entry system that is directly attached to a tube-well to treat As contaminated water.
409 The Apyron Technology Inc. As removal system contains highly activated hybrid alumina and
410 alumina composites which consist of enhanced pore and surface properties and it effectively
411 and selectively removes both As(III) and As(V) through both an inner and outer-sphere
412 complex formation which is a chemisorption process. The system was tested in Nepal for
413 providing safe water to the community. The test was conducted for eleven consecutive days
414 with this particular As removal system which was connected to an As contaminated tube-well
415 and showed excellent As removal throughout the eleven days. Already after the first day, the
416 effluent contained only 4 µg/L of As (influent 226 µg/L) and all rest of the nine days showed
417 As with below the detection limits in the effluent (306 µg/L of average influent concentration).
418 The advantages of the above system are that it can be used as a system for a community
419 (available for larger-scale), as the particular system with granular activated alumina metal
420 oxide is non-hazardous as it has non-leaching properties and therefore the exhausted media
421 (waste) can be disposed into a typical landfill. However, the cost is high (US\$2000 per unit)
422 and therefore, the use of such units in communities is a question (Hurd et al., 2001).

423

424 Luo et al. (2013) developed a novel hybrid adsorbent with hydrated zirconium oxide
425 nano-particles and graphite oxide, and a hydro-thermal co-precipitation reaction was employed
426 in the preparation of the hybrid adsorbent. The particular adsorbent was excellent for removal
427 of As(III) and As(V) simultaneously following Langmuir's adsorption equation and this
428 suggests the adsorption mechanism is an inner sphere formation. The removal dosages were
429 95.15 and 84.86 mg/g for As(III) and As(V), respectively, and the adsorption was applicable
430 for a wide range of pHs (pH 5-12 and 3-9, respectively). Moreover, the simultaneous removal
431 was far more effective for both As(III) and As(V) than separate removal by hydrated zirconium
432 oxide nano-particles graphite oxide. For both As(III) and As(V), among the interference
433 (bicarbonate, nitrate, sulfate, fluoride, and chloride ions), bicarbonate was insignificant while
434 the adsorption suppression occurred with phosphate ions (Luo et al., 2013).

435

436 Silica-based novel composite material has shown a selective affinity towards As(V) in
437 water (Awual et al., 2019). The fabricated $-NH_2$ derived highly porous composite material
438 operated well within the range of pH 3.5 to 7.0. The As(V) adsorption capacity of the composite
439 material was 142.25 mg/g at optimum conditions (initial concentration 75 mg/L) and it has
440 been tested in the presence of cations and anions to evaluate the selectivity aspect. With the
441 presence of chloride, bicarbonate, sulfate, sodium, calcium and magnesium ions (competing
442 ion concentrations were 20 times higher than those of As(V)), the As(V) adsorption was tested
443 and the monovalent anions and cations did not affect the As(V) adsorption (<3% removed from
444 those ions) but the divalent sulfate ions slightly interfered with As(V) adsorption (about 12%
445 of sulfate removed and slightly reduced the As(V) removal). Therefore, the particular
446 composite adsorption material has a selective affinity towards As(V); however, there is no data
447 for interference with phosphate (Awual et al., 2019).

448

449 Surface imprinting is one of the advanced techniques that has been used for selective
450 removal of As in water. Briefly, surface imprinting is a technique to immobilize the functional
451 groups onto the surface of supporting material (a polymer) to possess high selectivity towards
452 a target contaminant (Fan et al., 2012; Fang et al., 2018; Fu et al., 2015). 3-(2-
453 Aminoethylamino)propyltrimethoxysilane (AAPTS) is a kind of material that can be used to
454 surface imprinting in order to remove targeted pollutants (Chen et al., 2009). The AAPTS can
455 be used with silica and target certain metal ions with the functional group of $-\text{NH}-\text{CH}_2-\text{CH}_2-$
456 NH_2 (ethylenediamine). As(V) is one of the metalloids that have a high affinity towards this
457 functional group. The adsorption efficiency is dependent on the solution pH as the mechanism
458 for As(V) adsorption is the electrostatic effect. Within the range of pH 3-9, the adsorption
459 efficiency of AAPTS imprinted silica on As(V) is significant. The adsorption percentage is
460 almost 100% and throughout the 3-9 pH range, the adsorption capacity was similar. Below pH
461 9, the active functional group is NH_3^+ (after imprinting of AAPTS into silica) and As(V) exists
462 mainly as anions (H_2AsO_4^- and HAsO_4^{2-}). So, As(V) is adsorbed due to electrostatic effects.
463 As(III) is mostly found in neutral form and therefore As(III) adsorption cannot take place by
464 electrostatic forces. The co-existing cations such as K^+ , Na^+ , Ca^{2+} , Mg^{2+} , Al^{3+} , Zn^{2+} , Fe^{3+} , NO_3^-
465 and anions including SO_4^{2-} and Cl^- did not impact on the As(V) adsorption capacity however,
466 no data have been reported whether those ions were adsorbed or not with AAPTS imprinted
467 silica (Chen et al., 2009). Metal ion imprinting is a kind of surface imprinting technique and
468 silica gel is used mostly as the surface for selective removal of heavy metals (Fan et al., 2012).
469 As(V) imprinted amino-functionalized silica gel sorbent is used for selective removal of As(V)
470 in water. Here, the silica gel crosslinking has been completed in the presence of As(V) as a
471 template in order to specifically target the As(V) in water. Similar to most of the As(V) removal
472 methods, pH was one of the factors limiting the adsorption of As(V). The adsorption occurs

473 via a complexation mechanism through electrostatic effects in between As(V) and amino
474 functional groups. The pH range of 3.7-9 is the most efficient for As(V) adsorption while at
475 $\text{pH} < 3.7$ the H^+ ions compete with the adsorption sites. The material shows great selectivity
476 towards As(V) even in the presence of phosphate, Cd^{2+} , Cu^{2+} , and Pb^{2+} (Fan et al., 2012).
477 As(III)-ion imprinted polymer based on cyclic functional monomer is one of the surface
478 imprinted polymers that have been used on selective As(III) removal in water (Fang et al.,
479 2018). The cyclic functional monomer has been synthesized with a positively charged moiety,
480 tetra-bromine-bi-4, 5-2)methylene bi-imidazole) acridine and then the As(III) imprinted
481 polymer has been produced. The morphology analysis revealed that the produced novel
482 material has nanoscale particles and most of them have relatively homogeneous lamellar holes
483 structure. The novel material showed a maximum adsorption capacity of 55 mg/g at the 100
484 mg/L of initial As(III) concentration. The relative selectivity coefficient values for novel
485 material are 1.03, 1.95, 2.55 and 1.52 for chloride, sulfate, phosphate, and nitrate respectively
486 (Fang et al., 2018).

487

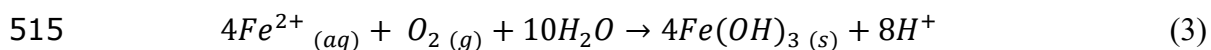
488 The adsorbent materials that have similar selectivity capabilities for both As(III) and
489 As(V) are rare, due to different chemistry of As(III) and As(V). A single-phase Fe/Mn oxy-
490 hydroxide shows equal selectivity on both As(III) and As(V) in drinking water (Tresintsi et al.,
491 2013). This particular nano-adsorbent material has been developed in a two-stage continuous
492 flow reactor. Briefly, the method of synthesis is coprecipitation of $\text{FeSO}_4 \cdot \text{H}_2\text{O}$ and KMnO_4 into
493 water. After the reaction in the flow-reactor, the received suspension has been washed and
494 centrifuged to separate the dry material. The material has been used as the adsorbent after been
495 ground into a fine powder ($< 63 \mu\text{m}$). With the XRD analysis, the developed fine powder shows
496 a nanocrystalline structure with a mean crystal size of 2 nm. The resultant adsorbent has shown
497 homogeneous distribution of Fe and tetravalent Mn at a nanoscopic level and therefore it has

498 been confirmed that there will not be any phase separation into pure MnO₂ and FeOOH phases.
499 The Mn(IV) responsible for oxidizing the As(III) into As(V) and As(V) adsorption occurs with
500 Fe atoms. However, there is no data to describe the behavior of As(III) and As(V) adsorption
501 with the presence of competitive anions (Tresintsi et al., 2013).

502

503 One of the successful field level As treatment units is community-scale As treatment
504 unit which show selective arsenic removal capabilities in the villages of West Bengal, India
505 since 1977 and one unit has the capability to provide water to an average of 150 families (Sarkar
506 et al., 2010; Sarkar et al., 2012; Sarkar et al., 2005). In accordance with increasing demand for
507 arsenic-safe water, the unit providing an excellent solution. Most importantly, the unit does not
508 require any electricity, chemical addition or pH adjustment for its operation. This community-
509 scale As treatment unit consists of a stainless steel column that has a volume of 100 L. The raw
510 water inlet is located at the top of the column and water enters through a spray head and splash
511 plates. At the raw water inlet, Fe(II) particles are stored and mixed with spray water, Fe(II)
512 contact with air and water and form fine precipitates of hydrated Fe(III) oxide with the
513 following reaction (Eq. 3).

514



516

517 Hydrogen ions generated in the process react with the alkalinity present in the
518 groundwater, with no notable pH change in the treated water. Freshly precipitated hydrated
519 Fe(III) oxide selectively adsorbs significant portions of both As(III) and As(V) in water with
520 the functional groups of FeOH₂⁺ and FeOH through Lewis acid-base interaction. The water in
521 the particular region contains high concentrations of chloride, sulfate and bicarbonate;
522 however, all three ions are weak ligands which have a poor affinity towards hydrated Fe(III)

523 particles. At the same time, phosphate and silica compete against As adsorption by the hydrated
524 Fe(III) oxide. The water then passes through a bed consisting of activated alumina or a hybrid
525 anion exchanger which can trap As as well as the released hydrated Fe(III) particles. The
526 desired water flow rate of the unit is 10-12 L/min (Sarkar et al., 2010).

527

528

529 **4.3. Selective removal of arsenic by modified ion-exchangers**

530 The conventional ion-exchange methods which are also mentioned in the introduction
531 section are not effective for removal of As and therefore several studies have attempted to find
532 the solution with modified ion-exchangers. Polymeric and inorganic ion-exchangers such as
533 chitosan and zeolite-based ion exchangers have been used as hosts for the development of
534 modified ion exchangers. The chemical and physical nature of the host material such as pore
535 size and distribution are also important for the enhancement of the removal capability of the
536 final product. Modified ion-exchange, therefore, has been identified as an effective method for
537 selective removal of As species from water. However, as stated in the introduction section, due
538 to different properties between the two principal As species (As(III) and As(V)) have different
539 behavior and adsorption mechanisms and act differently with modified ion-exchange methods.
540 For example, strong base anion-exchange resins have lack of selectivity towards As(V) in the
541 presence of sulfate and chloride ions whereas for As(III) adsorption the interference of sulfate
542 and chloride is not significant (Vatutsina et al., 2007). However, it should be noted that the
543 resin does not have a significant impact on As selectivity but its modification with some other
544 components e.g. Fe(III) oxide, can increase affinity to As. This fact has been tested by
545 Guenegou et al. (1998) using two different ion-exchangers (anion exchanger – packed with
546 AG1X-8 strong base anion exchange resin, cation exchanger – packed with AGMP-50
547 macroporous strong cation exchange resin) for As(III) and As(V) removal. The un-modified

548 two ion-exchangers alone were found insignificant for As removal; however, As removal was
549 remarkable after their modifications, especially, for As(III). Ramana and Sengupta (1992) have
550 studied a modified commercial anion exchange resin named Dow 2N. However, to improve
551 the selectivity towards As(V), the resin was modified by converting it into a copper-loaded
552 form by passing a Cu(II) solution following the principle of Lewis acid-base interaction by
553 creating a ligand exchanger. It has been identified that there are several drawbacks with Fe(III)
554 ions; and loading of Cu(II) instead of Fe(III) makes a much stronger Lewis acid which can
555 expect a greater As(V) loading capacity. By proving the assumed hypothesis, the modified
556 resin showed significantly higher selectivity towards As(V) despite the competition from the
557 sulfate. The As(V) which is an oxy-anion Lewis base comprising an electron donor and the
558 fixed Cu(II) sites in the resin was a Lewis acid which is the electron acceptor. A similar study
559 has been conducted for removal of As(V) from drinking water to test the selectivity of
560 modifying a commercial resin towards As(V) with the presence of sulfate. Copper loaded DOW
561 3N resin was tested for As(V) removal and the results proved that the modification could
562 enhance the As(V) selectivity so that it was 60-120 times greater based on the binary
563 arsenate/sulfate separation factor. After the adsorption experiment, the sulfate concentration
564 was the same as before. Moreover, the particular modified resin can be efficiently regenerated
565 with NaCl and it can be used in multiple cycles (8 cycles) without significant loss of removal
566 capacity (An et al., 2005). The porous structure of the anion exchangers provides space for
567 embedding nanoscale particles into the anion exchanger and this feature is beneficial in the
568 removal of a specific contaminant in water because the particular nanoscale inorganic particles
569 can selectively adsorb different contaminants. Further, there is another advantage of the
570 combined use of nano-particles with the anion exchange resin rather than when they are used
571 separately. The porous structure acts as a separation nano-reactor which helps to overcome the
572 agglomeration of the nanoscale particles. A zirconium molybdate embedded anion exchanger

573 developed by Bui et al. (2018) has been identified as having good selectivity towards phosphate
574 (Bui et al., 2018) and therefore, it could be used as a material for selective removal of As(V)
575 as well. Using the same adsorbent, the same research group has been working on As(V)
576 separately and the results showed excellent selectivity towards As(V) in the presence of up to
577 150:1 of SO_4^{2-} or NO_3^- :As(V) (90% removal of As(V)) (Bui et al., 2019). However, As(V)
578 removal in the presence of phosphate has not been assessed, so that further studies are required
579 before using a zirconium molybdate anion exchanger composite for As(V) removal in the
580 presence of phosphate.

581

582 Granulated ferric hydrochloride has been used widely for selective removal of As, but
583 it causes the release of As containing particles into the treated water (Vatutsina et al., 2007). It
584 has been identified that amorphous and crystalline hydrated Fe(III) oxides show significant
585 selectivity on As(III) and As(V) (Vatutsina et al., 2007). Therefore, amorphous crystalline
586 hydrated Fe(III) shows more advantageous characteristics towards selective removal of As over
587 granulated Fe(III). Arsenate adsorption by hydrated Fe(III) oxides occurs via inner-sphere
588 complex formation and As(III) forms both inner and outer sphere complex formation with
589 hydrated Fe(III) oxides (Figure. 2) (Goldberg and Johnston, 2001; Vatutsina et al., 2007; Zhao
590 et al., 2011). The basic mechanism behind the As(V) adsorption by hydrated Fe(III) is a ligand
591 exchange reaction between As anions and surface hydroxyl groups in the coordination sphere of
592 Fe atoms (Vatutsina et al., 2007). The particle size of the Fe(III) oxide also matters according
593 to its uses. The very fine submicron iron oxide or hydroxide particles have poor mechanical
594 strength and unacceptable durability. Such particles are unable to use in fixed-beds, permeable
595 reactive barriers or any flow-through systems. To overcome such barriers, Fe(III) oxide and/or
596 hydroxide particles can be encapsulated with robust polymeric support which can give an
597 excellent mechanical strength, durability and favorable hydraulic properties (Cumbal and

598 SenGupta, 2005; Iesan et al., 2008). There are several of such modified sorbents with hydrated
599 Fe(III) oxides considering their selectivity capability towards As species in order to improve
600 the adsorption capacities, mechanical properties as well as their hydraulic properties (DeMarco
601 et al., 2003; Greenleaf et al., 2003; Vatutsina et al., 2007). However, in anion exchangers with
602 incorporated Fe(III) oxide, the nature of the basic ion exchange matrix also matters for the
603 sorption capacity. The anion exchangers show higher sorption capacity for As compared to
604 those prepared with cation exchangers (Vatutsina et al., 2007). Further, weak base functional
605 groups containing ion exchangers are capable of higher As sorption than strong base functional
606 groups. Weak base ion exchangers are capable of loading larger amounts of Fe(III) oxides than
607 strong base ion exchangers. Moreover, weak base ion exchangers facilitate uniform and firm
608 loading of Fe(III) within the ion exchanger which is also a reason for their better As removal.
609 Additionally, the incorporation of Fe(III) oxides with ion-exchangers helps to avoid release of
610 fiber into the treated solution. Basically, As adsorption by iron-based sorbates interfere in
611 decreasing manner with phosphate > sulfate > chloride. However, Fe(III) oxide incorporated
612 ion exchangers show insignificant interference for both chloride and sulfate as Fe(III) oxide
613 has low affinity towards chloride and sulfate but high affinity towards As (Vatutsina et al.,
614 2007). As a consequence of the above findings, Vatutsina et al. (2007) have developed a fibrous
615 composite sorbent (commercially available FIBAN® ion-exchanger, based on a weak base) by
616 precipitation of Fe(III) oxide. This composite showed a high rate of As(III) and As(V) (~ 2.9 g
617 As/kg) adsorption which is in contrast to most of the ion exchangers that are used alone. Here,
618 90% of the As was adsorbed within 10 minutes (initial concentration 9 and 8.5 g/L of As(III)
619 and As(V), respectively). Moreover, the particular composite sorbent did not release any Fe
620 into the contacting solution and did not require any backwashing step in column studies which
621 is advantageous and is economically friendly. The arsenic adsorption capacity of this composite
622 anion exchanger depends on pH. At the low and high pH ends (for As(III) pH<6, pH>10 and

623 for As(V) pH<4, pH>9), the sorption capacity decreases significantly. Dissociation of H₃AsO₄
624 and H₃AsO₃ is the major reason for this lower adsorption and additionally, at acidic pH levels
625 the hydrated Fe(III) oxide particles dissolve and at higher pH levels they become inactive for
626 As sorption. However, the active pH level is within the range of natural water and therefore, it
627 does not require any prior pH adjustment. The interference of chloride and sulfate is
628 insignificant for the composite sorbent developed by Vatutsina et al. (2007). However,
629 phosphate has a negative influence on the adsorbance of As(V) but no influence on As(III).
630 According to the literature, at the mild acidic condition, the As(III) adsorption becomes higher
631 but not for As(V). The main reason is that phosphate has the ability to effectively compete with
632 As(V) sorption sites of Fe(III) oxide particles as both of them are adsorbed via inner-sphere
633 complex formation (Vatutsina et al., 2007). At an As(V)/phosphate ratio of 1, the As adsorption
634 (0.6 mmol/mmol Fe) is higher than the phosphorous adsorption (0.4 mmol/mmol Fe)
635 (Vatutsina et al., 2007). However, considering the natural conditions, the phosphate
636 concentration is far higher than the As concentration; therefore, selective As adsorption is again
637 a problem.

638

639 A hybrid sorbent has been tested by DeMarco et al. (2003) and it could remove both
640 As(III) and As(V) in a selective manner. The particular hybrid sorbent contains spherical
641 macro-porous polymeric cation exchanger beads within submicron hydrated Fe(III) oxide
642 particles. The nano-scale hydrated Fe oxide particles have been uniformly and irreversibly
643 dispersed, employing a simple chemical-thermal treatment. The experiment has been done as
644 a fixed-bed column and most importantly, the hybrid ion exchanger can be regenerated for
645 further use. The regeneration of the material is also an easy process (with 10% NaOH). Due to
646 the weak acid-base properties of Fe(III) oxide (hydrated metal ions) they have a high affinity
647 towards hydroxyl ions. Therefore, the ligand sorption can be greatly reduced at the alkaline pH

648 and further it causes desorption of the ligands from the negatively charged functional groups
649 of hydrated metal ions following the Donnan co-ion exclusion effect (Sarkar et al., 2012).
650 Moreover, cost-effectiveness is also advantageous compared with most other As removal
651 methods, since the raw materials are available worldwide (DeMarco et al., 2003).

652

653 Another anion exchange base hybrid adsorbent was developed and named HFO/SBA
654 (Iesan et al., 2008). It was obtained by in situ encapsulation of ferric hydroxide into the macro-
655 porous structure of a strong base anion exchange resin based on a styrene-divinylbenzene
656 copolymer, employing a simple thermal treatment. In a fixed-bed column study, the HFO/SBA
657 adsorbent showed good adsorbance capacity towards As(V) with 15.26 mg As/g dry adsorbent.
658 Some other anions such as sulfate, chloride, nitrate and bicarbonate did not affect As(V)
659 adsorbance but phosphate and silicate decreased the As(V) adsorption by 2.59 (17%) and 5.19
660 mg As/g (34%) dry adsorbent, respectively, and in presence of all these ions together, As(V)
661 adsorption capacity was reduced by 50%. Further, the particular hybrid sorbent was able to
662 remove As(III) as well but the capacity of removal (~5.5 mg As/g dry adsorbent) is less than
663 that of As(V). With the presence of 80 and 20% of As(V) and As(III), respectively, the removal
664 capacity was 14.07 mg As/g dry adsorbent which is a decrease of less than 10%. Moreover, the
665 optimum As removal is pH 5 which is the lowest pH among the tested pH values (pH 5, 7 and
666 9). The HFO/SBA adsorbent also has regeneration and reuse capability for As removal (Iesan
667 et al., 2008).

668

669 Another material for selective As removal is macroporous sulfonic acid resin (Bio-Red
670 AGMP-50). The modified resin has been produced by the precipitation of ferric hydrochloride
671 into the above mentioned commercially available resin (Guenegou et al., 1998; Mohanty,
672 2017). The adsorbent was selective for both As(III) and As(V) with the presence of chloride

673 ions. However, there were no reported data for interference with other potential competitive
674 ions. It has been reported that the macroporous anion-exchanger was effective at As(III)
675 removal after being modified with Fe-Mn binary oxide (Li et al., 2012). However, it is
676 important to note that the anion-exchanger was dissimilar to that described by Mohanty (2017).
677 The added advantage of the Fe-Mn binary oxide was that it can simultaneously oxidize As(III)
678 into As(V) and adsorb As(V) in water. The anion exchanger itself was used to enhance the
679 applicability of Fe-Mn binary oxide and introduce the Donnan membrane principle. The
680 modified anion exchanger works well in low pH ranges (4-6.5) and this pH range is preferable
681 for both of oxidation (As(III)) and adsorption (As(V)). The anions which are potentially
682 competing for adsorption sites, chloride and sulfate, did not reduce the As(V) adsorption
683 significantly but phosphate and silicate showed significant adsorption loss at high
684 concentrations; phosphate showed the greatest adsorption loss for As(V) (by 60% at 10 mM of
685 phosphate) (Li et al., 2012).

686

687 The ligand exchange based As treatments methods are available for selective removal
688 of As. The polymeric ligand exchange comprises a cross-linked hosting resin which binds with
689 a transition metal such as iron and copper, as well as metal ions and metalloids that are
690 immobilized to the functional groups of the resin. This polymeric ligand exchanger is very
691 similar to the standard ion exchanger but the ligand exchanger uses transition metal ions as its
692 terminal functional groups. As a result of these terminal functional groups, the ligand
693 exchangers have Lewis acid-base interactions and the electrostatic interactions between the
694 fixed metal ions and the target ionic ligands (An et al., 2005). Ligand exchange named
695 iminodiacetic chelating resin (Chelex 100) in ferric ion form selectively removed both As(III)
696 and As(V) ions and the saturation capacities were 70 and 45 mg As/g wet resin, respectively
697 (Table 1) (Chanda et al., 1988). The resin can be regenerated and most importantly, after

698 regeneration, the sorption capacity has not decreased. (Chanda et al., 1988). Zr(IV) loaded
699 adsorbents have been proven to efficiently adsorb As(V) through ligand exchange mechanisms
700 (Dambies, 2005; Suzuki et al., 2000). Another advantage of Zr(IV) loaded fibrous material is
701 its ability to take up trace levels (0.015 mM) of As(V) from water, even at high feed flow rates
702 (750 h^{-1}), which is an ability that most of the metal loaded ligand exchangers do not have
703 (Awual et al., 2012). Following this phenomenon, a Zr(IV) loaded monophosphonic acid resin
704 showed selective adsorption properties towards As(V) through a ligand exchange mechanism
705 (Awual et al., 2019). Since Zr(IV) is a hard Lewis acid, the As(V) adsorption depends on the
706 solution pH. In other words, at high pH levels (>7), the Zr(IV) adsorbs mostly the hydroxyl
707 ions and at acidic pH levels, the adsorption capacity for As(V) is high. Therefore, the Zr(IV)
708 loaded monophosphonic acid resin works well at the pH range of 2-7. The presence of chloride
709 and sulfate do not interfere with the As(V) adsorption but only shift the breakthrough curves
710 to the right. This particular modified resin has been tested for both As(V) and phosphate and a
711 higher affinity towards phosphate than to As(V) has been found. Therefore, the Zr(IV) loaded
712 monophosphonic acid resin alone will not be able to act selectively for As(V) if there is a
713 similar or higher concentration of phosphate than of As(V). However, the modification of
714 Zr(IV) loaded resin with phosphonate and sulfonate groups enhanced the selective As(V)
715 removal capacities (Awual et al., 2012). The Zr(IV) loaded resin removed 0.005 mmol/g of
716 As(V) in the presence of Cl^- and SO_4^{2-} and a similar resin including phosphonate and sulfonate
717 groups could selectively remove 0.119 mmol/g of As(V) (feed concentration is 2 mg As(V)/L)
718 (Awual et al., 2019; Awual et al., 2012). The main function of the introduced phosphonate and
719 sulfonate functional groups was to make proper binding of Zr(IV) into the resin so that more
720 Zr(IV) particles can be packed within the resin which can enhance its adsorption capacity and
721 overcome the removal of Zr(IV) particles from the resin with the treated flow. However, studies
722 have not been reported to assess the adsorption pattern of As(V), with the presence of

723 phosphorus in the raw water which is one of the most important competitive ions for adsorption
724 and needs to be assessed. In the recent literature there are several studies that have attempted
725 to remove As with Zr based adsorbents; however, the selective removal aspect is missing in
726 those studies. A highly porous material comprising nanostructured ZrO₂ spheres is such an
727 adsorbent that showed exceptional As(III) and As(V) removal in fixed bed experiments. It
728 could remove 9.2 mg/g of As(III) and 9 mg/g of As(V) at the initial concentration of 0.212 and
729 0.335 mg/L, respectively (Cui et al., 2013). The above mentioned Zr based adsorbents that
730 showed selective adsorbance were only for As(V), but the ZrO₂ spheres based adsorbent
731 showed removal capability for both As species and it is worth studying its capability for
732 selective As removal.

733

734 These examples show that conventional ion-exchangers have a great affinity for As
735 removal with the incorporation of Fe(III) particles. However, in general, most of the resins are
736 not economically feasible and therefore, the availability of other, more economic methods for
737 selective As removal is vital. Considering this fact, Muñoz et al. (2002) have prepared a non-
738 conventional ion-exchange material as an economical method which is based on an open-celled
739 cellulose sponge (to avoid release into the water phase) incorporating a chelating polymer with
740 selective affinity for contaminants, e.g. As (Forager sponge). The material has been selected
741 due to the presence of amine and iminodiacetate groups which are the groups that can interact
742 with heavy metals and metalloids (anions and cations) by chelation and ion-exchange. The
743 selectivity behavior toward As has been obtained by incorporation of Fe(III). The As
744 adsorption capacity is 0.35 mmol As/g (13.3 mmol/L of initial concentration and 0.16 g of dry
745 sponge). The interference of anions is in the order of phosphate > sulfate > nitrate > chloride
746 and the interfering effect is significantly lowered with chelating polymer forage sponge when
747 compared to the cellulose sponge used alone.

748

749

750 **4.4. Selective arsenic removal by bio-sorbents based methods**

751 The bio-sorbents are possible materials that have been used and can be used in the As
752 removal processes. The biochemical composition of the bio-sorbents contains different kinds
753 of functional groups such as hydroxyl, carboxyl, and amide which can remove As in water
754 through complexation (Shakoor et al., 2019). Further, one of the major requirements of any of
755 the contaminant removal processes is lowering the cost and bio-sorbents are great options in
756 relation to economic and environmental cost. Moreover, the process is simple and easy to
757 operate. However, due to low efficiency compared to the above-mentioned adsorbents, very
758 few attempts are found in literature based on bio-sorbents for selective As removal. Chitosan
759 is an example of a bio-sorbent and a potential adsorbent, especially for transition metals as it
760 consists of amino and hydroxyl groups (Kwok et al., 2014). Many attempts can be found in the
761 literature for the use of chitosan without modification (Kwok et al., 2009; Kwok and McKay,
762 2010) and modified chitosan for the removal of As in water. Some examples of the modified
763 chitosan are chitosan beads impregnated with molybdate (Chassary et al., 2004; Chen et al.,
764 2008) and chitosan beads impregnated with titanium (Miller et al., 2011; Miller and
765 Zimmerman, 2010). Chitosan itself does not have specific ability to selectively remove As but
766 the modification of chitosan with selective adsorption features will allow its use in selective
767 As removal. Although chitosan is not a good adsorptive material and has no selectivity, as well
768 as having insufficient mechanical strength, it provides a high surface area for trapping the
769 contaminant in water. Moreover, with the amine and hydroxyl groups on the polymer
770 backbone, easy functionalization is facilitated with favorable functional groups for the targeted
771 contaminant. Therefore, those advantages overcome the weak mechanical strength, allowing
772 chitosan to be used in the preparation of composite materials (Pincus et al., 2019). While

773 considering the advantages of chitosan, different composites can be found. Pincus et al. (2019)
774 and (Pincus et al., 2018) have developed a composite material including chitosan and nano-
775 metal oxides. Nano-metal oxides are good adsorbents but difficult to recover, resulting in high
776 costs. Moreover, integrating nano-metal oxides into chitosan has overcome the drawbacks of
777 both chitosan and nano-metal oxides when used individually. Nano TiO₂ has been used as
778 nano-metal oxide with chitosan. Apart from adsorption, nano TiO₂ has the ability to cause self-
779 oxidation of As(III) and complete the removal process. For selective removal of As, Cu(II) has
780 been incorporated and the selective removal capabilities have been tested with multifunctional
781 nano-TiO₂-Cu(II)-chitosan material. It has been identified that Cu(II) has the potential to
782 enhance the selectivity in engineered adsorbents (Ramana and Sengupta, 1992). In engineered
783 adsorbents, Cu(II) acts as an electron acceptor and can also form a complex with oxyanions
784 (Yamani et al., 2016). The multifunctional material is able to remove 3.2 mg/L (84%) of
785 As(III) (initial concentration 3.8 mg/L) under UV irradiation and the presence of phosphorous
786 as a competing ion in the solution only lowered it by 0.83 mg/L (22%). However, nano TiO₂
787 alone removed only 2.2 mg/L (58%) of As(III) and in the presence of phosphate ions, only
788 0.38 mg/L which is a 48% reduction. Therefore the multifunctional material showed excellent
789 improvement with As removal capacity and selectivity for As. Yamani et al. (2016) produced
790 chitosan-Cu(II) beads to assess As(V) removal with the presence of phosphate as the
791 competitive anion. Cu(II) has the ability to bind with chitosan at several electron-donating
792 sites, such as amine and alcohol on the chitosan backbone, depending on the system's
793 condition. At pH levels lower than 5.5, the Cu(II) ions bind with amine groups on chitosan,
794 making type-1 complexes (Fig. 3). The higher Cu(II) loading does not make any difference in
795 the chitosan-Cu(II) complexes. With the pH levels higher than 5.5, first, the chitosan and Cu(II)
796 make type-1 complexes but with increased Cu(II) loading, type-II complexes are formed (Fig.
797 3). Therefore, at pH levels higher than pH 5.5 there will be a mixture of type-I and type-II

798 complexes (Rhazi et al., 2002; Yamani et al., 2016). The complexed Cu(II) is then able to open
799 up binding sites for oxyanions (Yamani et al., 2016). Both As(V) and phosphate show
800 increasing adsorbency with increasing Cu(II) in the system which is due to increased binding
801 sites of the chitosan-Cu(II) beads. There is 25-35% of As(V) adsorbency reduction when the
802 phosphate is present in the solution (1:10 As(V):PO₄³⁻). At low Cu(II) loading, the As(V)
803 adsorption is limited while phosphate adsorption shows nearly linear behavior. The data
804 demonstrates that there is a Cu(II) loading threshold level for obtaining higher As(V)
805 adsorption over phosphate. The adsorption mechanism suggests that phosphate facilitates
806 binding with type-I chitosan-Cu(II) beads while As(V) facilitates binding with type-II (Yamani
807 et al., 2016). If there is a method to obtain chitosan-Cu(II) beads that have only type-II
808 complexes the As(V) adsorption can be maximized, avoiding the impact of phosphate; further
809 studies are needed on this regard.

810

811 Another chitosan-based bio-sorbent, a furfuraldehyde-chitosan cross-linked hydrogel,
812 also shows selective affinity towards As(V). The particular hydrogel has stability in a broad
813 range of pH (1-8) and adsorbs 100% of As(V) from groundwater which has 15 µg/L of As(V).
814 The material shows high As(V) selectively in the presence of Cd(II), Cr(III), Ni(II) and Pb(II)
815 (Maity et al., 2019). Shinde et al. (2013) have tested composites developed using chitosan and
816 different metal ions for selective As(V) pre-concentration, using Cu(II), Fe(III), La(III),
817 Mo(VI) and Zr(IV). Among those metal complexes, Fe(III)-chitosan and La(III)-chitosan show
818 better and more significant As(V) sorption compared to other complexes and those two
819 composites are able to remove 95% of As(V) from the aqueous solution at the range of pH 3-
820 9. Comparing La(III)-chitosan and Fe(III)-chitosan, the latter is better in selective As(V)
821 adsorption. As(V) is a borderline hard base (hard Lewis base) and therefore reacts with hard
822 or borderline acids. Regarding La(III) and Fe(III), the latter is harder than La(III). So, the

823 interaction is stronger between As(V) and Fe(III) compared to As(V) and La(III). Therefore,
824 Fe(III) is one of the best metal ions for sorption of As(V). The Fe(III)-chitosan has also been
825 used for treating As(V) containing seawater (Shinde et al., 2013). After the As adsorption, a γ -
826 ray study shows that there is only the As peak in the spectrum. Therefore, the selective As
827 removal by Fe(III)-chitosan has been confirmed. A novel material has been developed using
828 chitosan and zerovalent iron, known as zerovalent iron encapsulated chitosan nano-spheres
829 (Gupta et al., 2012). The use of chitosan is for enhancement of mechanical stability and
830 durability of Fe(0) nanoparticles. The developed sorbent reduces the As concentrations from 2
831 mg/L of As(III) and As(V) to lower than 5 $\mu\text{g/L}$ obeying Langmuir monolayer adsorption
832 behavior and the adsorptive properties are useful for a wide range of pH (pH 2-9). The
833 selectivity towards As(III) and As(V) is significant even in the presence of major ions such as
834 sulfate, phosphate, and silicate. The adsorbent is available for reuse and has been successfully
835 applied for removal of real groundwater which contains both As(III) and As(V) (Gupta et al.,
836 2012). Another material that has been developed based on chitosan is Fe-Mn binary oxide
837 impregnated chitosan beads (Qi et al., 2015). The preparation of this novel sorbent employs
838 two steps which are powdered Fe-Mn binary oxide synthesis and Fe-Mn binary oxide
839 impregnated chitosan beads fabrication. The Fe-Mn binary oxide impregnated chitosan beads
840 show excellent selective sorption capacities for both As(III) and As(V), obeying Freundlich's
841 equation and sorption of As(III) is high compared to As(V). The sorption capacities are 39.1
842 and 54.2 mg/g for As(V) and As(III), respectively. The optimum sorption is in the range of pH
843 6-8. With the increase of pH beyond this range the adsorption decreases. The adsorption
844 capacity of Fe-Mn binary impregnated chitosan beads is not significantly influenced by
845 coexisting ions such as bicarbonate, silicate and sulfate; however, the presence of phosphate
846 ions suppresses the As(III) and As(V) adsorption. The material can be regenerated for reuse.
847 Although the adsorption amount decreases with the increment of regeneration cycles it is not

848 significantly lower compared to the fresh material. The adsorption capacity is 85%, even with
849 the fourth regeneration cycle (Qi et al., 2015).

850

851 It has been noted that thiol groups pose high affinity towards As in aqueous media but
852 the studies are limited in this regards (Singh et al., 2016; Singh et al., 2018). A novel material
853 has been prepared with chitosan, thiol and Fe(III) that has high affinity for both As(III) and
854 As(V) in aqueous media (Singh et al., 2018). Generally speaking, removal of As(III) requires
855 peroxidation (Ezeh and Harrop, 2012) but the thiol groups and As(III)/As(V) interact with
856 Lewis acid-base interaction and remove both As(III) and As(V). For providing extra
857 coordination sites for As(III) and As(V) binding, the chitosan-thiol has been incorporated and
858 the results have been significant. The particular chitosan-thiol-Fe(III) composite showed rapid
859 As(III) and As(V) sorption within the first 60 mins (about 60-65%). The chitosan provides a
860 large surface area for a large number of thiol functional groups and Fe(III) oxide and therefore,
861 such rapid adsorption has taken place. After 3 hours the As(III) adsorption is 99.5% and As(V)
862 adsorption is 99% (initial concentration 50 µg/L). Without the introduction of Fe(III) into
863 chitosan-thiol material, the adsorption percentages are 85% and 87%, respectively (Singh et
864 al., 2016). Therefore, Fe(III) oxide provides a significant amount of binding sites for both
865 As(III) and As(V). The composite material poses a heterogeneous surface for effective As(III)
866 and As(V) adsorption. The surface of Fe(III) oxide provides space for binding of chitosan-thiol
867 and As(III)/As(V). Further the thiol groups in the chitosan act as binding sites for As(III) and
868 As(V). The SEM image confirms that no bare space is found on the composite material and
869 therefore the adsorption is occurring in an effective manner. The impact of competing anions
870 also has been studied and the results reveal that Cl⁻, NO₃⁻, and SO₄²⁻ show a negligible effect
871 while PO₄³⁻ reduces the adsorption by 37.5% for As(III) and by 34% for As(V) (Singh et al.,
872 2018).

873

874

875 **4.5. Selective arsenic removal by membrane filtration/permeable reactive barrier**

876 **methods**

877 The membrane-based methods such as reverse osmosis are economically feasible for
878 water that has a trace amount of contaminant. Except for a few cases, most often the As
879 contamination found with trace levels (less than 500 µg/L) and the reverse-osmosis method is
880 practicable for As removal (Sarkar et al., 2012). The reverse-osmosis method on As removal
881 has been identified as highly effective but these require large operating pressure and energy
882 which increase the cost of the process and reduce the efficiency of the process (Chang et al.,
883 2014; Fox et al., 2016). The forward osmosis, however, requires low-pressure and has low
884 fouling tendencies (Xu et al., 2017; Yang et al., 2019; Zhao et al., 2012). However, the basic
885 forward osmosis technique with thin selective layer is not efficient enough for removal of As
886 in water to meet the WHO recommended levels (Jin et al., 2012; Mondal et al., 2014a). Grafting
887 of ionic liquids on to the thin selective layer has been identified as a potential modification to
888 overcome the fouling process and gain higher rejection rates for As while ensuring maximum
889 water flux. Yang et al. (2019) developed and grafted a series of bi-functional imidazole-based
890 ionic liquids onto a thin-film (thin polyamide selective layer) composite forward osmosis
891 membrane. The grafting process was done following a simple amidation grafting procedure
892 following incorporation of ionic liquids with amine functional groups. The synthesized
893 composite membrane showed higher electronegativity and stronger electrostatic repulsion with
894 As oxyanions and is less prone to fouling. The As(V) rejection was 99.5% at the pH 11. At the
895 alkaline pH values, the neutral H_3AsO_4^- is gradually converted into higher valance As
896 oxyanions, enhancing the mutual repulsion between the negatively charged ionic membrane
897 and As oxyanions. Therefore, it enhanced the As(V) rejection rates. The presence of competing

898 ions such as NO_3^- and SO_4^{2-} reduced the As(V) rejection rates slightly (nearly 5%). The
899 presence of competing ions increased the feed osmotic pressure, reducing the net driving force
900 across the membrane which can reduce water flux and the As(V) rejection rates. Moreover, the
901 repulsion of larger ions such as NO_3^- and SO_4^{2-} (hydrated radius – 0.34, 0.34 nm respectively)
902 by the negatively charged membrane could enable smaller HAsO_4^{2-} (hydrated radius – 0.20
903 nm) to pass through the membrane interior and this will enhance the fouling process which
904 reduces the water flux and As(V) rejection rates (Mondal et al., 2014b; Yang et al., 2019).

905

906 The concept of permeable reactive walls or barriers exists mainly for the removal of
907 dissolved contaminants in the water while ensuring regular water flow in either groundwater
908 or surface water (Liao et al., 2018). A pilot study has been conducted in China to avoid/lower
909 the As contamination of lake Yangzonghai (average 177 $\mu\text{g/L}$), Yunnan by surface runoff input
910 sources (average 140 $\mu\text{g/L}$). The permeable reactive barrier has been developed by
911 modification of zeolite by ionic liquids. The field-scale ionic liquid modified zeolite has been
912 mixed with the ratio of 1 ton zeolite:50 kg of 70% ionic liquid in a concrete mixer. The ionic
913 liquid modifying a zeolite permeable reactive barrier has been installed in a valley near
914 Yangzonghai lake. In batch sorption studies the As (total As) removal was 11 and 17 mmol/kg
915 (824 and 1273 mg/kg) for the particle ranges of 0.35-1 and 1.0-1.41 mm respectively. A study
916 with Fe-exchanged zeolite showed in batch sorption studies 6-8 mg/kg sorption of As(III) and
917 As(V) (Li et al., 2011) which was much lower than the ionic liquid modified zeolite. The best
918 pH range for the above As sorption by ionic liquid modified zeolite was 1-6 and the surface
919 water it was treated with was in the range of 5-6. Without pH adjustment the water could be
920 treated and could achieve the optimum removal capacity. The suggested mechanism for As
921 removal by ionic liquid modified zeolite is surface anion exchange. The removal of counterion
922 Cl from the modified zeolite surface confirms the suggested mechanism. In the six months of

923 the testing period with permeable reactive barrier the As removal rate was nearly constant with
924 an average removal of 96%. In May 2016 the As concentration at the upper stream of permeable
925 reactive barrier was 0.14 mg/L and after passing through the permeable reactive barrier the As
926 concentration was 0.004 mg/L with 96% removal. In August 2016 the As concentrations were
927 0.51 and 0.02 mg/L respectively with 96% removal (Liao et al., 2018). However, there is no
928 data regarding selectivity behavior of the ionic liquid modified zeolite permeable reactive
929 barrier.

930

931

932 **4.6. Selective arsenic removal by microbiological methods**

933 The use of microorganisms is achieving increasing interest in different industries such
934 as food and beverages, cosmetics, pharmaceuticals and energy. However, regarding As
935 removal in water and wastewater, the use of microorganisms is still a novel aspect (Abbas et
936 al., 2014; Hayat et al., 2017; Merrifield et al., 2004; Shakoori et al., 2010; Singh et al., 2008).
937 The use of microorganisms in As removal has several advantages; for example, they can be
938 produced in fast and in large quantities. Moreover, genetic engineering can be applied to
939 improve the qualities and introduce the desired properties (Hayat et al., 2017). A marine alga
940 named *Fucus vesiculosus* (a seaweed species) has been identified as being As tolerant.
941 Scientists cloned the *F.vesiculosus* to *Escherichia coli* and after cloning the *F. vesiculosus*
942 expresses as a fusion protein in *E. coli*. It has been identified that *F. vesiculosus* bound *E. coli*
943 has a high affinity for As(III) in vitro (Singh et al., 2008). Moreover, to improve the selectivity
944 toward As(III), an As(III) transporter has been co-expressed with *F. vesiculosus* bound *E. coli*
945 (Figure 2). After allowing the prepared materials for As removal which contained 10 mM of
946 As(III) and As(V) separately the *F. vesiculosus* bound *E.coli* could remove 6.91 mmol/g of
947 As(V) and 6.08 mmol/g of As(III). After co-expression of As(III) transporter to *F. vesiculosus*

948 bound *E. coli*, it could remove 8.61 mmol/g of As(III) which confirms the enhancement of As
949 removal. Moreover, the impacts of co-existing ions were tested with the incorporation of Zn²⁺,
950 Cd²⁺, and Pb²⁺ into initial solution. The interference of Pb and Zn was negligible, ensuring
951 selective As removal by *F. vesiculosus* bound *E. coli*. However, Cd could suppress the As(III)
952 accumulation by 56% but with As(III) transporter the impact was reduced by 30%. Most
953 importantly even the resting cells in the engineered strain could accumulate and remove As
954 with the absence of nutrients and antibiotics. The removal efficiencies were the same as the
955 growing cells and they could remove trace levels of As in water and therefore the method is
956 suitable to meet the USEPA guidelines in drinking water (Singh et al., 2008).

957

958

959 **5. Conclusion and future perspectives**

960 Selective removal of As in aqueous solutions is a challenge due to several reasons. In
961 most cases, the common anions present in natural waters or wastewater, which are generally
962 present in much higher concentrations are competing with As adsorption. Moreover, with
963 changing solution pH and the redox potential in the media, the As changes into different
964 oxidization forms, including As(V) oxyanions and neutral As(III) species, in most of the natural
965 waters, which physically and chemically act in different ways and therefore, there exists no
966 single removal method which can remove all of the As species satisfactorily at the same time.
967 However, it has been identified that hydrated granular or amorphous Fe(III) has significant
968 capability to remove As(III) and As(V) in aqueous solutions in a selective manner. To improve
969 mechanical strength and adsorption capacities, there are attempts with the incorporation of
970 mechanically strong materials with hydrated granular or amorphous Fe(III). Chitosan and ion-
971 exchange resins are examples of this. The firm deposition of hydrated granular or amorphous
972 Fe(III) in the used matrix is an important step in the preparation procedure to improve the

973 selective As removal. Instead of Fe(III), there are some metal ions such as Cu^{2+} , La^{3+} , and Al^{3+}
974 that have been used for selective As removal and they also show significant As removal
975 capabilities. There is no single material that can be used for selective As removal material
976 which is pH-independent. Therefore, the pH of the solution is a limiting factor for selective As
977 removal by any of the selective As removal material. However, most of the selective As
978 removal materials are suitable within pH 6-8 range which is the range for most natural waters.
979 Moreover, there is evidence to show that microbial methods for selective As removal in
980 aqueous media. Most of the co-existing anions such as sulfate, nitrate, bicarbonate, chloride or
981 fluoride do not interfere with As removal with most of the selective As removal materials.
982 However, phosphate adversely impacts As removal of many of the methods. The reason is that
983 phosphate ions have the same chemical structure as As and it is chemically compatible with
984 the As. One of the important aspects is the chitosan and Cu(II) integration can form two types
985 of bonds and the two types of bonds remove As and phosphate separately. The fact is both
986 bonds present as a mix and there is a research gap to optimize the conditions in order to have
987 only the particular bond that can remove the As. Even though phosphate is also removed with
988 most of the selective As removal measures, the selective As removal in natural water is an
989 important achievement. In most of the cases, the phosphate concentrations are much lower than
990 those of the main ions. Therefore, the above mentioned selective As removal methods are still
991 highly beneficial to overcome the global As contamination issue. In consequence, more studies
992 are needed to overcome the interference of phosphate with As removal, especially for the water
993 resources that have high phosphate concentrations. Thiol based removal methods even have
994 the ability to target on specific As species when there are both As(III) and As(V). Moreover,
995 the high affinity of thiol groups towards As species have greater future perspective in the
996 selective As removal field, even to minimize the competition from phosphate. If such affinity
997 could combine with the Cu(II) and chitosan it may even avoid the phosphate competition.

998 However, more novelty and studies can be developed using such advantageous characters.
999 Even though there are microbial methods to remove As in a selective manner, the studies have
1000 not extended to testing the interference of phosphate with As removal. Therefore, more studies
1001 are needed with extended scope in microbial methods to use and selective As removal strategy.
1002 If the microbial methods are strong enough to compete with phosphate, the incorporation of
1003 both chemical and microbiological methods may overcome the interactive issues with common
1004 ions and further studies are needed to test the possibility of the use of chemical and
1005 microbiological methods together.

1006

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1009

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