*Review Article*

# A Comparative Study on Removal of Hazardous Anions from Water by Adsorption: A Review

**Yasinta John ⬤,[1] Victor Emery David Jr. ⬤,[1] and Daniel Mmereki[2]**

[1]*College of Urban Construction and Environmental Engineering, Chongqing University, Chongqing 400044, China*
[2]*National Centre for International Research of Low-Carbon and Green Buildings, Chongqing University, Chongqing 400045, China*

Correspondence should be addressed to Yasinta John; john_yasinta@yahoo.com

This paper presents a comparative review of arsenite (As(III)), arsenate (As(V)), and fluoride (F⁻) for a better understanding of the conditions and factors during their adsorption with focus on (i) the isotherm adsorption models, (ii) effects of pH, (iii) effects of ionic strength, and (iv) effects of coexisting substances such as anions, cations, and natural organics matter. It provides an in-depth analysis of various methods of arsenite (As(III)), arsenate (As(V)), and fluoride (F⁻) removal by adsorption and the anions' characteristics during the adsorption process. The surface area of the adsorbents does not contribute to the adsorption capacity of these anions but rather a combination of other physical and chemical properties. The adsorption capacity for the anions depends on the combination of all the factors: pH, ionic strength, coexisting substances, pore volume and particles size, surface modification, pretreatment of the adsorbents, and so forth. Extreme higher adsorption capacity can be obtained by the modification of the adsorbents. In general, pH has a greater influence on adsorption capacity at large, since it affects the ionic strength, coexisting anions such as bicarbonate, sulfate, and silica, the surface charges of the adsorbents, and the ionic species which can be present in the solution.

## 1. Introduction

Hazardous anions are another group of pollutants in drinking water in addition to metal ions and organics which are known to be toxic and carcinogenic. The presence of these anions in ground and surface waters has resulted in severe contamination and has caused adverse health effects. Among the toxic anions, arsenite (As(III)), arsenate (As(V)), and fluoride (F⁻) have shown concern in the treatment of wastewaters and drinking water. Adsorption process among several treatment technologies is applied for removal of fluoride (F⁻), arsenite (As(III)), and arsenate (As(V)) ions due to the availability of local material and being easy to operate and maintain and in general it is a low-cost technology and is suitable for use in developing countries. The adsorption process is influenced by several environmental conditions, such as pH, salt effect, or ionic strength, the presence of other anions, cations, and organic matter, and adsorbate physical and chemical properties which have been reported in previous studies [1–5]. However, no previous study was done to compare the two

anions based on the influence factors such pH, salt effect, or ionic strength and the presence of other anions and their relationship on the adsorption isotherm. This review aims to present an evaluation of these parameters and their effects on arsenite (As(III)), arsenate (As(V)), and fluoride (F⁻) by adsorption process on different adsorbents. It also seeks to find the relationship between the anions and their influencing factors. Therefore, this review focuses on the isothermal adsorption models, the effects of the pH and ionic strength, and the impact of coexisting substances including anions and cations to show the characteristics of fluoride (F⁻), arsenite (As(III)), and arsenate (As(V)) anionic adsorption processes.

*1.1. Arsenic.* Arsenic is discharged into the environment by natural activities and anthropogenic activities [6, 7]. Arsenic occurs in both organic and inorganic forms. Arsenate (As(V)) and arsenite (As(III)) are the inorganic forms of arsenic which are considered to be more toxic and are more prevalent in water. The existence of arsenic species depends on the pH

solution and redox conditions [8]. The ingestion of inorganic arsenic can result in both cancerous and noncancerous health effects. An arsenic concentration less than 0.05 mg/L in chronic exposure has been linked to skin diseases, neurological and cardiovascular system disorder, and skin, kidney, and lung cancer [6, 9, 10]. Arsenic affects physiological activities, such as the activities of essential cations, enzymes, and transcriptional events in cells [6, 9]. Elevated concentrations of arsenic in drinking water have also been reported to cause an increase in abortions and stillbirth [11].

The methods of arsenic removal from water include oxidation and filtration, adsorption, biological oxidation, coprecipitation, and membrane technologies [12]. Numerous arsenic treatment technologies require pH adjustment and are useful in removing arsenic in the pentavalent state. Thus oxidation is included as a pretreatment to convert As(III) to As(V) [13]. However, the process of coagulation and flocculation produces sludge, which makes it inefficient for As(III) removal [13]. Adsorption process with a wide range of adsorbents has been proven to be effective for the adsorption of arsenate (As(V)) and arsenite (As(III)) ions from water and has been reported by various researchers [14–16].

*1.2. Fluoride (F⁻).* The contamination of fluoride in groundwater has been known worldwide to cause severe human health problems [17, 18]. Fluorides exist with iron, aluminum, and beryllium as fluoride ion ($F^-$) in natural waters [19]. It is caused by the discharge of mineral sediments and industrial (production of phosphate fertilizers (3.8% fluorine), bricks, tiles, and ceramics) effluent which contains fluoride in receiving water bodies [19]. The inorganic fluorine compounds are used in industry for aluminum production and as a flux in the steel and glass fiber, fluorosilicic acid, sodium hexafluorosilicate, and sodium fluoride are used in public water fluoridation treatment [18]. Fluoride is also essential in human health as the component for normal mineralization of bones and formation of dental enamel [20].

Fluoride is beneficial in drinking water at levels up to 0.7 mg/L but is harmful above 1.5 mg/L, according to the World Health Organization limit [21]. The excessive intake of fluorides may result in dental and skeletal fluorosis [20]. Fluorosis is prevalent in more than 20 developed and developing nations [20, 21]. Fluorides can also cause arthritis, infertility osteoporosis, brain damage cancer, Alzheimer syndrome, thyroid disorder, and brittle bones [17, 21]. High fluoride concentrations are known to interfere with carbohydrates, lipids, proteins, vitamins and mineral metabolism, and gastrointestinal irritation when by initially, acting on the intestinal mucosa, and then form hydrofluoric acid in the stomach at a later stage [17, 20]. Fluoride can also cause kidney disease in both animals and humans and interfere with the functions of the brain and pineal gland [17].

Due to the toxic effects of fluoride in human health, various methods have been developed for the removal of excess fluoride ions from drinking water. Currently, the common methods include adsorption into activated alumina (AA), bone char, and clay [22], precipitation with lime, dolomite, and aluminum sulfate, Nalgonda technique [23], ion exchange and reverse osmosis, electrodialysis, and nanofiltration [22]. The coagulation, adsorption, and ion-exchange techniques are widely opted as defluoridation techniques practiced in fluoride endemic areas [23]. The Nalgonda technique and adsorption by bone char have been used in many developing countries like Tanzania and India [23]. However, the disadvantages of this technique were reported by some researchers, for example, higher residual aluminum concentration (2–7 mg/L) in treated water than WHO standard of 0.2 mg/L [17]. The membrane processes provide good-quality water but have a higher cost of operation [23].

## 2. Adsorption Method for Arsenic and Fluoride Removal

Adsorption methods have been proven to remove fluoride and arsenic up to 90% from water [16, 22]. However, in adsorption process, the constituents of adsorbents are at large accountable for the elimination of pollutants [24, 25]. Many adsorbents are used in adsorption process, but the most common ones in the treatment of both water and wastewater are activated carbon, activated alumina, ion-exchange resins, metal oxides, hydroxides, carbonates, and clays [16, 22]. The adsorption process is described through equilibrium isotherm which occurs when an adsorbate comes in contact with the adsorbent for a period of time. Thus, the concentration of adsorbate in the solution is balanced with the interface concentration [25]. Equilibrium isotherm is essential for the effective design of sorption systems [26].

The adsorption capacity of the various adsorbents is influenced by pH, the existence of other adsorbing anions, ionic strength, temperature, properties of the adsorbents, initial concentration of the adsorbates, and so forth [16, 17]. Experimental results showed that the pH solution is the main controlling parameter in the adsorption processes [27]. pH affects adsorption by affecting the surface charge on the adsorbent [4, 24, 28, 29]. However, the evaluation of pH effects is governed by the specific interactions between the ions and the adsorption sites [30]. The adsorption of anions decreases by increasing pH due to the higher concentration of competitive anions, such as $OH^-$ and increases due to protonated surfaces. In aqueous solution, the adsorption process is primarily governed by the zero point charge (ZPC) of an adsorbent [31, 32]. At zero point charge, the pHzpc is the characteristic that determines the pH at which the adsorbent surface has net electrical neutrality. It is also where the acidic or basic functional groups no longer contribute to the pH of a solution [33]. At pH values above the ZPC, the surface has a net negative or anionic charge, and the surface would take part in cation attraction, as well as cation exchange reactions. The surface has a net positive charge at pH values below the ZPC. Therefore, it will attract anions USEPA [34]. Metal adsorption's dependence on pH is related to the nature and ionic state of the functional group existing in the adsorbent and the metal chemistry in the solution [35–37].

Many studies have been conducted on fluoride removal by using adsorption [22] and arsenic [16]. Moreover, pH has been reported to be a key factor affecting fluoride adsorption at the water adsorbent interface [38]. It has been reported that the removal of fluorine ions occurs between pH of 2.0

and 8.0 [27, 39, 40]. Also, the adsorption of arsenic species is highly dependent on pH due to its ability to exist as As(III) or As(IV) at different pH values. As(III) is highly removed at higher pH (basic) value, while As(IV) is removed in acidic pH and rapidly decreases in basic medium [41–43].

The adsorption capacity of the adsorbents is also influenced by the physical and chemical characteristics of the adsorbent [16]. The surface area and total pore volume determine the adsorption capacity based on the results of the kinetics and equilibrium on adsorption experiments [44–47]. The control of chemical and physical oxygen functional groups considerably affects their performance on the adsorption process [47]. However, the use of Extended X-ray Absorption Fine Structure (EXAFS), Fourier transform infrared spectroscopy (FTIR), and X-ray absorption near edge structure (XANES) has been employed for the removal of fluoride [48] and arsenic [49] to further study the adsorption mechanism and involvement of functional groups in different adsorbents. These have revealed the involvement of functional groups like hydroxyl and carbonates in the surface, which participate in the adsorption.

Different materials exist in water and wastewater, which have different absorption properties and may compete with each other for the limited amount of sites adsorption, and therefore the adsorption in the specific material is reduced [4, 50, 51]. These materials include anions and cations and organic matters [51–55]. Anions such as sulfate, nitrate, carbonate, chloride, bicarbonate, and phosphate influence adsorption by adjustment of the electrostatic charge at the solid surface because of the same negative ions [11, 56–61]. The effects of anions on fluoride removal were reported by [40, 62–66]. Both direct and indirect effects of these anions are influenced by pH, anions' concentrations, and intrinsic binding affinities [42, 59]. One of the common interfering anions is phosphates. Phosphates exist in four different forms depending on the pH value, phosphate ion ($PO_4^{3-}$), dihydrogen phosphate ion ($H_2PO^{4-}$), and hydrogen phosphate ion ($HPO_4^{2-}$) in dilute aqueous solution and in aqueous phosphoric acid ($H_3PO_4(aq)$) [60]. $PO_4^{3-}$ ions are more predominant in strongly basic conditions, $HPO_4^{2-}$ ions in weakly basic conditions, $H_2PO^{4-}$ ions in weak acidic condition, and aqueous $H_3PO_4$ [60]. In general, $SO_4^{2-}$, $NO_3^-$, and $Cl^-$ interfering ions have shown an insignificant effect on adsorption of these anions compared with $HPO_4^{2-}$ and $HCO_3^-$, which have a great impact in all anions adsorption [16, 67].

The effects of cations like $Al^{3+}$, $Fe^{3+}$, $Mg^{2+}$, $Ca^{2+}$, and $Mn^{2+}$ in adsorption and their interference with the adsorption capacity of these anions have been reported by [56, 62, 68–71]. The presence of cations like $Ca^{2+}$ and $Mg^{2+}$ increases the fluoride with increasing $Ca^{2+}$ and $Mg^{2+}$ concentration [72]. Ionic strength has been reported to increase with an increase in adsorption for arsenate [67] and it has no significant effect on the adsorption of fluoride [73].

Natural organic matter in water may delay sorption equilibrium and decrease the extent of arsenite and arsenate adsorption [16]. Natural organic matter contains a mixture of weak organic acids and organic compounds which

do not have a clear chemical structure [50]. Fulvic acids (FA) and humic acids (HA) are hydrophobic in nature, and they represent almost 60% of the dissolved organic in aquatic systems [56]. Humic substances interfere with anionic adsorption through stable metal complex formations [23, 54, 56]. Due to the importance of these parameters in adsorption process, we evaluated the adsorptions isotherms, coexisting substances, the effects of pH, and ionic strength and their effects on arsenite (As(III)), arsenate (As(V)), and Fluoride ($F^-$) removal on different adsorbents and aimed to find the relationship between them. The insight of anion adsorption in water basically confined to the adsorption of a single ion and on the specific adsorbent. Therefore this review summarizes the common characteristics of anions adsorption and explains the roles for the relevant forces and the adsorption control conditions and features of the adsorbents suitable for the arsenite (As(III)), arsenate (As(V)), and fluorine ($F^-$) adsorption in water.

## 3. Adsorption Isotherm Studies on As(III) and As(V)

Freundlich isotherm, Langmuir isotherm, and BET isotherm are examples of the most frequently used isotherm models in adsorption process [25, 26, 37, 52]. In this review, only Freundlich and Langmuir were taken into consideration due to their wide applicability to gain an insight into the degree of the favorable adsorption [74].

Adsorption technology can reduce arsenic concentrations to less than 10 mg/L [75], and the common sorbents for arsenic removal are commercial and synthetic activated carbons, agricultural products and by-products, and industrial waste soils and constituents, for example, clay minerals, manganese dioxide, zeolite, activated alumina, ferrihydrite/iron and hydroxide/iron oxides, hydroxides, hydrotalcites, phosphates, and metal-based methods, for example, zerovalent iron [13, 16]. Iron-based sorbents (IBS) have been reported as promising adsorbents for arsenic removal, since they have higher affinity for arsenic under neutral conditions [76]. These include activated ferric oxide or ferric hydroxide and iron-coated sand [13]. The removal of arsenic by using iron-based adsorbents occurs through adsorption to a surface hydroxyl group, coprecipitation, and ion exchange [77]. However, with the iron oxides adsorbents, the removal of As(V) at neutral pH occurs through ligand exchange by the formation of monodentate complexes at low surface coverage, while at high surface coverage, As(V) species bind to the oxides through the formation of bidentate complexes while occupying two adsorption sites at the same time [78]. Few activated carbons are selective for the adsorption of As(III) and As(V) in concentrations <0.5 mg/L from water [51].

As(V) can be easily removed by a wide range of adsorbents compared to arsenic (III) (Table 1) and because arsenic (III) is easily adsorbed to arsenic (V) and is oxidized before or during the adsorption process. As(III) oxidation occurs naturally or by using iron, hydrogen peroxide, chlorine, hypochlorite, and manganese, as shown in a study conducted by Giles et al. [79]. Also, another reason is the fact that adsorption of arsenic significantly depends on arsenic speciation, which

TABLE 1: Adsorption isotherm for arsenic.

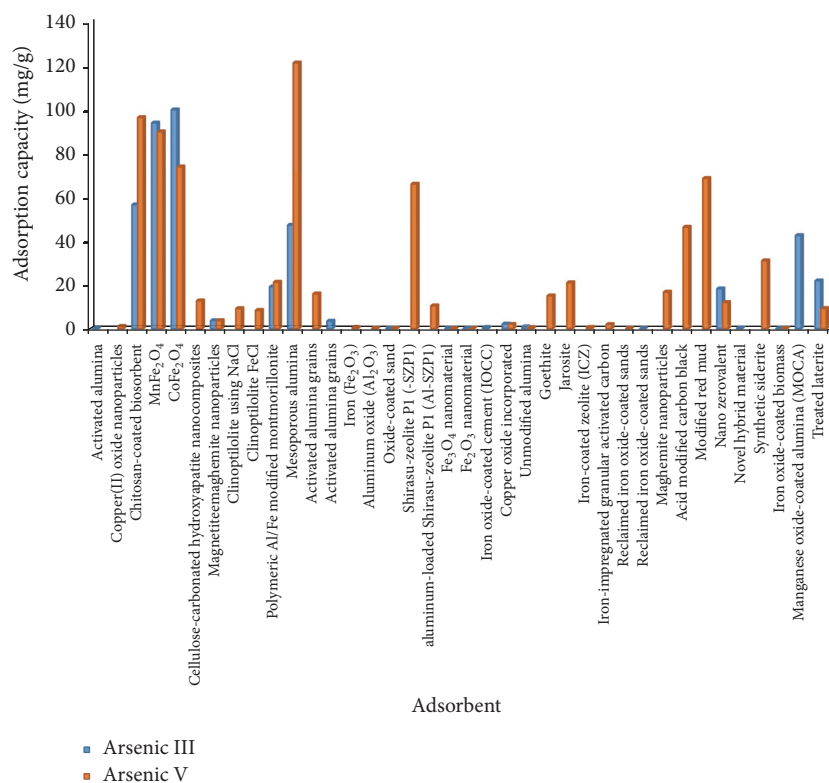| Adsorbent | Adsorption capacity | | Adsorption isotherm | Initial concentration | References |
| --- | --- | --- | --- | --- | --- |
| | Arsenic III | Arsenic V | | | |
| Zirconium Polyacrylamide hybrid (ZrPACM-43) | 0.20 mg/g 0.80 mg/g | | Freundlich | 10 mg/L | [14] |
| Manganese oxide-coated alumina (MOCA) | 42.48 mg/g | — | Sips | — | [2] |
| Nano zerovalent | 18.2 mg/g | 12 mg/g | Freundlich and Langmuir | — | [3] |
| $MnFe_2O_4$ | 94 mg/g | 90 mg/g | Langmuir | 10 mg/L | [42] |
| $CoFe_2O_4$ | 100 mg/g | 74 mg/g | Langmuir | 10 mg/L | [42] |
| Manganese(II, III) oxide ($Mn_3O_4$) | | 101 $\mu g/m^2$ | Langmuir Freundlich | 1 mg/L | [52] |
| Activated alumina | 0.0545 mg/g | — | Langmuir, Freundlich | 0.5 mg/L | [82] |
| Copper(II) oxide nanoparticles | — | 1.0862 mg/g | Langmuir | 100 $\mu g/L$ | [57] |
| Chitosan-coated biosorbent | 56.5 mg/g | 96.46 mg/g | Langmuir | 100 ppm | [83] |
| Cellulose-carbonated hydroxyapatite nanocomposites | | 12.72 mg/g | Langmuir | 10 mg/L | [84] |
| Magnetiteemaghemite nanoparticles | 3.69 mg/g | 3.71 mg/g | Freundlich | 1.5 mg/L | [85] |
| Polymeric Al/Fe modified montmorillonite | 19.11 mg/g | 21.23 mg/g | Freundlich | 10 mg/L | [86] |
| Activated alumina grains | — | 15.9 mg/g | Langmuir | 2.85 and 11.5 mg/L | [87] |
| Activated alumina grains | 3.48 mg/g | | Langmuir | 0.79 and 4.90 mg/L | [87] |
| Iron ($Fe_2O_3$) | — | 0.66 mg/g | Langmuir | 200 $\mu g/L$ | [60] |
| Aluminum oxide ($Al_2O_3$) | — | 0.17 mg/g | Langmuir | — | [60] |
| Oxide-coated sand | 0.0411 mg/g | 0.0426 mg/g | Langmuir | 100 $\mu g/L$ | [88] |
| Shirasu-zeolite P1 (-SZP1) | — | 65.93 mg/g | Freundlich | — | [89] |
| Aluminum-loaded Shirasu-zeolite P1 (Al-SZP1) | — | 10.47 mg/g | Freundlich | 0.13 mM | [89] |
| Alum-impregnated activated alumina (AIAA) | — | 0.0314 mmol/g | Langmuir | 1–25 mg/L | [90] |
| Copper oxide incorporated | 2.161 mg/g | 2.017 mg/g | Langmuir | — | [91] |
| Unmodified alumina | 0.925 mg/g | 0.637 mg/g | Langmuir | — | [91] |
| Goethite | — | 15 mg/g | Langmuir | — | [92] |
| Jarosite | — | 21 mg/g | Langmuir | — | [92] |
| Iron-coated zeolite (ICZ) | — | 0.68 mg/g | Langmuir | — | [93] |
| Iron-impregnated granular activated carbon | — | 0.6 mg/g and 1.95 mg/g | Langmuir | — | [93] |
| Reclaimed iron oxide-coated sands | 6.7–8.7 g/g | — | Langmuir | 301 g/L | [94] |
| Maghemite nanoparticles | — | 16.7 mg/g | Langmuir | — | [95] |
| Acid modified carbon black | — | 46.3 mg/g | Langmuir | 100 mg/L | [96] |
| Modified red mud | — | 68.5 mg/g | Langmuir | — | [69] |
| $MnO_2$-modified natural clinoptilolite zeolite | — | 1 $\mu g/g$ | Freundlich | 20 $\mu g/L$ | [97] |
| Unmodified natural clinoptilolite | — | 0.38 $\mu g/g$ | Freundlich | 20 $\mu g/L$ | [97] |
| Novel hybrid material | 0.25 mg/g | | Langmuir | 10 mg/L, 50 mg/L, and 100 mg/L | [98] |
| Synthetic siderite | — | 31 mg/g | Langmuir | | [99] |
| Iron oxide-coated fungal biomass | 880 $\mu g/g$ | 1080 $\mu g/g$ | Langmuir | 100 g/L | [100] |
| Cupric oxide nanoparticles | 26.9 mg/g | 22.6 mg/g | Langmuir isotherm | | [101] |

FIGURE 1: Comparison of the adsorption capacity for arsenic removal.

also depends on pH and potential. Modified adsorbents have been shown to have a higher capacity for arsenic adsorption (Figure 1) compared to unmodified adsorbents. The modified adsorbents include, but are not limited to, acid modified carbon black, modified red mud, chitosan-coated biosorbent, bimetal oxide magnetic nanomaterials ($MnFe_2O_4$ and $CoFe_2O_4$), polymeric Al/Fe modified montmorillonite, manganese oxide-coated alumina and synthetic siderite. During arsenic adsorption, surface area is insignificant (Figure 2) and does not contribute to the adsorption capacity of the adsorbents [30, 76, 80]. The equilibrium adsorption capacity depends on the concentration of ionic species in solution and the sorbent properties [30]. The choice of the adsorbents to agree with Langmuir or Freundlich is still unclear. However, a study by [81] suggested that if As(V) followed Freundlich isotherm on arsenic adsorption onto Iron-Zirconium Binary Oxide-Coated Sand (IZBOCS), it showed that the adsorption of As(V) followed multilayer and heterogeneous adsorption process. Langmuir model was the best fit for As(III) and As(V) adsorption on iron–aluminum hydroxide coated onto macroporous and, according to the author, the adsorptions occur through chemisorption.

Studies by using X-ray photoelectron spectroscopy (XPS) have revealed that As(III) was oxidized and absorbed in the form of As(V) on the surface of cupric oxide nanoparticles (CuO) [101]. FTIR spectroscopy has also been used to elucidate the arsenic adsorption mechanism on iron mineral oxide which involves ligand exchange reactions where the anions displace $OH^-$ and $H_2O$ from the surface [102]. Fourier

transform infrared (FTIR) spectra demonstrated that Ca–OH functional group was involved in As(V) removal of bone char and coprecipitation and ion exchange was involved before and after As(V) adsorption [103]. Another study suggested that the adsorption of As(III) occurs through electrostatic attraction on bismuth-impregnated biochar [104]. Similar results were obtained by [105] on arsenic adsorption on feldspars, but the electrostatic attraction was between the luminol function groups and predominant form of arsenate in low pH. Another EXAFS analysis concluded that the adsorption of As(III) and As(V) on iron–aluminium hydroxide coated onto macroporous was involved through formation of inner-sphere complexes to the iron hydroxide. However, for As(III) adsorption, the bidentate complex was formed, which corresponded with the pseudo-second-order kinetic model [106].

The adsorption of As(V) anions on activated carbon was associated with the concentration of hard acid functional groups and not the carbon surface area [30]. Similar results were reported by [80] on arsenic adsorption on hydrous ferric oxide. Figure 2 shows that adsorption capacity of various adsorbents does not depend on the surface area for arsenic removal. However, it has been reported that changes in the type of arsenic complex binding with the surface area depend on pH and the number of available sites for adsorption for specific adsorbents [80]. In arsenic ions adsorption, pore diffusion is important, since the particle size, solubility, pH, and metal ions concentration affect adsorption capacity and the adsorption capacity increases with a decrease in particle size [76, 107].
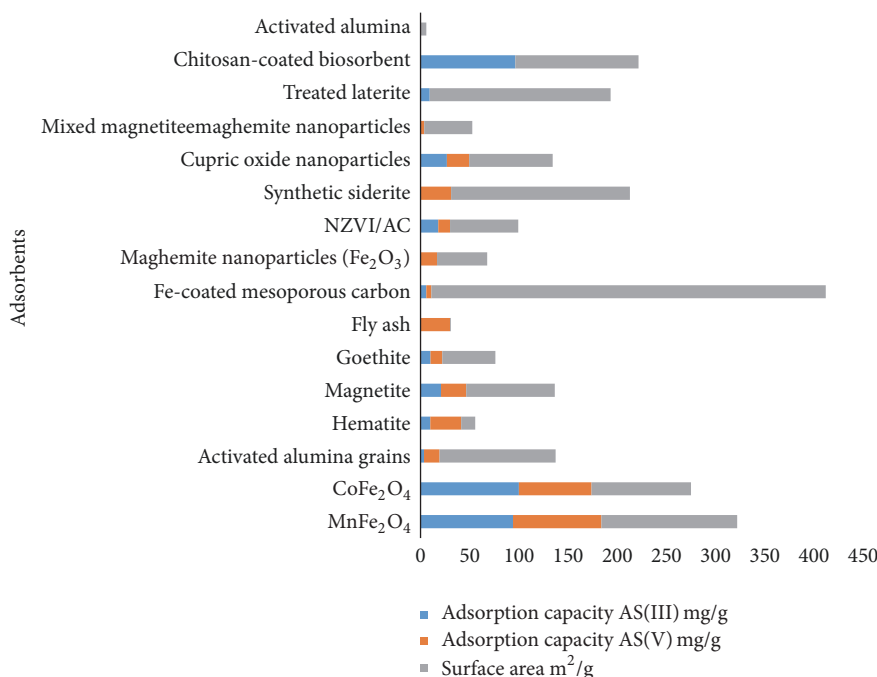
FIGURE 2: Adsorbents sorption capacity and surface area for arsenic removal.

Hassan et al. [108] investigated arsenic removal on potassium hydroxide activated carbon-based apricot stone, calcium alginate beads, and calcium alginate/activated carbon composite beads. The adsorbents materials have surface areas of $1621 \, m^2/g$, $32.9 \, m^2/g$, and $733.6 \, m^2/g$ and the adsorption capacity at $20°C$ was $26.3 \, mg/g$, $39.4 \, mg/g$, and $54.8 \, mg/g$, respectively. The authors concluded that the As(V) adsorption depends largely on pH, surface chemistry of solid adsorbent, and textural properties of the adsorbate besides its surface area. Another study by using magnetic graphene oxide as an adsorbent for arsenic removal showed that initial concentration of arsenic and the adsorbent dosage were the major factors affecting the adsorption capacity [109].

A maximum adsorption capacity of $3.1 \, mg/g$ was reported for activated carbon prepared from oat hulls which has a specific area of $522 \, m^2/g$ at initial arsenic concentrations of 25 to $200 \, \mu g/L$ [110]. Similarly, a low adsorption capacity for adsorbents with a high surface area was observed by Roy et al. [111] on thioglycolated sugarcane carbon (TSCC) as an adsorbent for arsenic removal. TSCC has a surface area of $5690 \, m^2/g$. The maximum reported As(III) and As(V) removal by TSCC was 85.01 and $83.82 \, \mu g/g$, respectively, with an initial arsenic concentration of $1,500 \, \mu g/L$ [111].

Low surface areas with high adsorption capacity have also been observed in numerous research works. For example, the removal of As(V) and As(III) from water by a Zr(IV)-loaded orange waste gel had an initial concentration of $20 \, mg/L$ and surface area of $7.25 \, m^2/g$. The maximum adsorption capacity of the Zr(IV)-loaded sol-gel was $88 \, mg/g$ and $130 \, mg/g$ for As(V) and As(III), respectively [112]. Similar results were reported by [83] on chitosan-coated biosorbent and by [14] on zirconium polyacrylamide hybrid material (ZrPACM-43). A high adsorption capacity has also been reported

for an adsorbent with a high surface area. For example, Liu et al. [113] investigated arsenic adsorption on $Fe_3O_4$-loaded activated carbon prepared from waste biomass with surface area of $349 \, m^2/g$; a very high adsorption capacity of $204.2 \, mg/g$ was observed with arsenic initial concentration of $40 \, mg/L$ [113]. With the reported observation, selection of adsorbent for arsenic adsorption should be based not only on surface area of the adsorbent but also on the combination of chemical properties of the adsorbent and adsorbate.

## 4. Effects of pH on Arsenic Removal

Removal of arsenic from water depends on pH as the adsorption capacity changes with changes in pH. The reduced trivalent form of arsenic (arsenite (As(III))) primarily exists in natural waters and anaerobic environment, while arsenate (As(V)), an oxidized pentavalent form, is found in aerobic environment conditions such as surface waters [79]. Arsenate species exist as $AsO_4^{3-}$, $HAsO_4^{2-}$, and $H_2AsO_4^{-}$ and arsenate species exist as $As(OH)_3$, $As(OH)_4^{-}$, and $AsO_3^{3-}$ depending on the pH solution [114]. Chemical speciation affects arsenic removal in aqueous solution (USEPA) [115]. As(V) exists as a charged species in water across a wide range of pH while As(III) exists as a charged species across a much narrower range of pH [16, 42, 87, 89, 116, 117], and it has been reported that many adsorbents prefer to adsorb charged species [16]. Arsenite (As(III)) is uncharged (i.e., $H_3AsO_3$) at natural pH levels (6–9) (Figure 3); thus it it difficult to remove compared to charged arsenate (As(V)) (i.e., $H_2AsO_4^{-}$ or $HAsO_4^{2-}$) (USEPA) [115]. As(III) is oxidized to As(V) by an oxidizing agent such as chlorine or permanganate in most arsenic treatment processes [79, 89]. Adsorbents like iron-based and
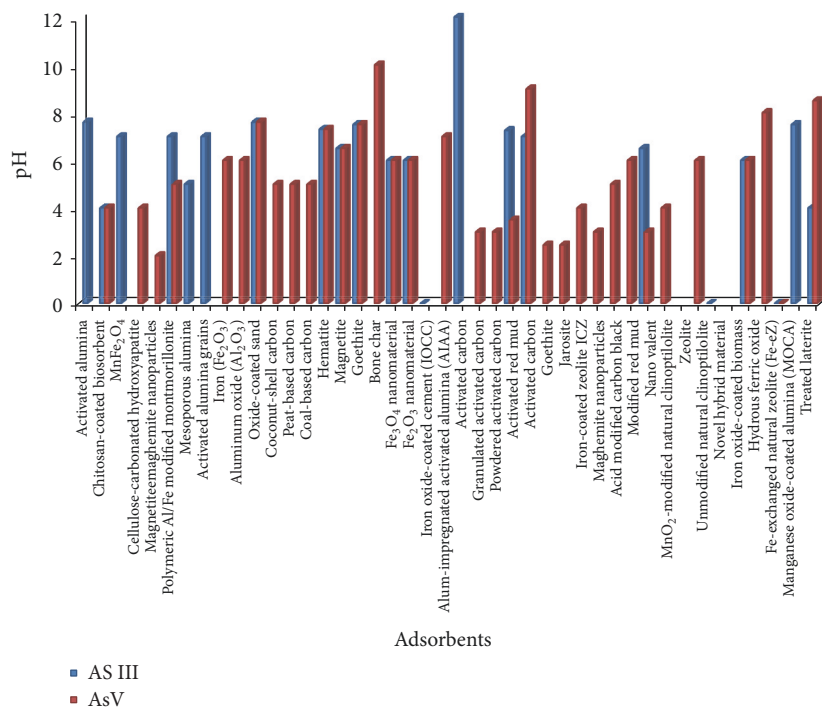
FIGURE 3: Effects of pH on As(V) and As(III).

iron minerals are characterized by their point of zero charges at a certain pH, where the mineral surface charge is equal to zero [42, 50, 84]. However, in other adsorbents, the strong adsorption of arsenic at pH > pHpzc indicates that the adsorption process is influenced by surface complexation and not electrostatic interaction [86].

Arsenate and arsenite adsorption onto activated alumina was governed by both the surface charge of activated alumina and the form of arsenic species in the water. Since alumina is sensitive to pH, adjustment of pH is done prior to treatments. Therefore, the adsorption of arsenite (As(III)) is much less than that of arsenate (As(V)) for activated alumina in most pH conditions, because arsenate is present in the negatively ionic state and arsenite is in nonionic state. For example, Singh and Pant [82] studied the removal of As(III) by activated alumina (AA), and the result showed that 94.4% maximum adsorption was reached in the pH range of 6.0–8.0 and it decreased at higher pH values [82]. Similar results were observed by [80, 87].

A study by Mamindy-Pajany et al. [118] on adsorption of As(V) on commercial hematite and goethite as a function of pH (2 to 12) and ionic strength showed that As(V) adsorption was higher at low pH value and insignificant at higher pH values. Similar results were reported by [119] on As(V) adsorption on goethite from aqueous solution and [120] on As(III) and As(V) adsorption on hematite, magnetite, and goethite. However, hematite was reported to be the appropriate adsorbent for As(V) removal in natural medium because it can exist at a wide pH range [99]. Mamindy-Pajany et al. [121] observed a similar trend on As(V) adsorption by hematite but, for As(III), the adsorption was highly dependent on

initial pH, and a decrease in adsorption was observed at the pH value of 3.

The adsorption of As(III) and As(V) has also been reported to be affected by pH higher than 10. For example, a study of As(III) and As(V) ions to the $Fe_3O_4$ nanomaterial [70, 122] observed similar trend on an iron oxide-coated cement (IOCC) adsorption capacity of As(III) removal and [123] on activated carbon. Also, a high adsorption percentage was observed at higher pH for As(V) adsorption over activated charcoal and bone char adsorbents. Adsorption of As(V) has been reported to be maximum at low pH values. Ansari and Sadegh [123] reported a maximum adsorption of As(V) at pH of 3 and decreased with the decrease of pH. That is, adsorption by activated carbon is thought to be carried out through anion exchange process and physicochemical adsorption due to the highly porous structure of activated carbon. The surface of the activated carbon has a positive charge under acidic conditions, where these positive charges are balanced with their associated anions. Therefore, these anions can be exchanged with the other anionic species present in the solution. Arsenic (III) adsorption on synthetic siderite has also been related to electrostatic attraction as well as physicochemical reactions [124]. In general, As(III) is adsorbed at neutral pH (Figure 3) and As(V) at a wide range of pH (2–10) depending on the adsorbent material used. A similar trend on arsenic adsorption by various adsorbents was reported by [50, 57, 60, 103].

Another different result on effects of pH on As(V) has been reported by [83] on removal of arsenic (III) and arsenic (V) from aqueous medium using chitosan-coated biosorbent (CCB), whereby a decrease in pH increases

As(V) adsorption and the mechanisms involved in As(V) removal were ionic attraction, nodule formation, and absorption.

## 5. Effects of Coexisting Anion, Cation, and Organic Matter on Arsenic

*5.1. Effects of Coexisting Anions.* Coexisting anions such as $Cl^-$, $NO_3^-$, $SO_4^{2-}$, $CO_3^{2-}$, and $PO_4^{3-}$ ions, in water sources, might compete with arsenic for active adsorption sites and significantly reduce the arsenic removal performance by the adsorbents. These coexisting anions have been reported to form inner-sphere complexes with arsenic and reduce the interaction between the two anions. The effects tend to be significant with a change in pH and with the increase of the anions concentration [3, 78].

*5.1.1. Sulfate.* Arsenic removal using $KMnO_4$–Fe(II) showed that, in the presence of 50–100 mg/l of sulfate, adsorption of arsenic was reduced by 6.5–36.0% over pH 6–9. The reasons were the competition for surface sites, the weak affinity of arsenic to the adsorbent, and the mechanisms for the adsorption of arsenic and sulfate being not the same. Guan et al. [56] studied the adsorption of arsenic into hydrous ferric oxide, and the results showed a decreasing trend on adsorption of As(III) after the pH was less than 4 [58]. A similar trend was observed by [60] on As(V) removal by iron oxide and aluminum oxide and by [92] on arsenic removal by goethite and jarosite in acidic conditions. However, Maiti et al. [50] showed that sulfate ion did not have any effect on As(V) and As(III) ions adsorption due to higher adsorption affinity of treated laterite surface on As(V). A similar result was observed by [42, 125].

*5.1.2. Phosphate.* The effect of phosphate is different for both As(III) and As(V). The decrease in adsorption capacity of the adsorbents is more for As(III) at lower concentration and As(V) at higher concentration. However, the influence of phosphate is also affected by pH. Arsenic removal using $KMnO_4$–Fe(II) showed that arsenic removal was reduced by 29.8%, 34.2%, and 47.3% at pH of 4, 5, and 6, respectively, in the presence of phosphate. The reasons were the competition of arsenate and phosphate for binding sites and inhibition of forming Fe precipitates and reduction of surface sites [56]. And, by increasing phosphate concentration to 2.5 mg/L, the arsenic removal was reduced by 59.6% [56]. As(III) and As(V) removal from water by copper oxide-incorporated mesoporous alumina showed that the presence of phosphate significantly reduces the As(V) adsorption due to the competition between phosphate and As(V) [45, 91]. Jeong et al. [60] reported that the increase of phosphate concentration decreases As(V) adsorption capacity on the adsorption of As(V) by $Al_2O_3$ compared to $Fe_2O_3$. A similar observation was reported by [89] on aluminum-loaded Shirasu-zeolite as an adsorbent. Arsenic adsorption was reduced by more than 20% when phosphate concentration increased by more than 0.2 mM on copper (II) oxide nanoparticles as adsorbents [57]. Maiti et al. [50] reported that arsenic was reduced to 72.9% removal when phosphate concentration was increased

to 5 mg/L on synthetic siderite as an adsorbent for As(V) removal. However, at low concentration of 0.2 mg/L phosphate on Fe(VI)/Al(III) chloride salts, arsenic removal was reduced to 73% [61].

*5.1.3. Silicate.* In natural water, silicate originates from the weathering of minerals and is always dissolving and precipitating at the earth's surface. Silicate is usually oxyanions in natural water, with their concentration between 0.45 and 14 mg Si/L [56, 60]. A 50% arsenite removal reduction was observed on Fe(VI), Fe(VI)/Fe(III), and Fe(VI)/Al(III) salt as adsorbent for arsenite removal in presence of 10 mg Si/L [61], whereas with 10 mg Si/L silicate concentration showed no effect with $KMnO_4$–Fe(II) as adsorbent at pH 5, but adsorption was observed to be decreased by 42% at pH 9 [56]. Therefore effects of silicate on arsenic removal are more obvious with an increase in pH and can be associated with the weak silicic acid species distribution with pH [56]. Similar results were reported by [60] on adsorption of As(V) on $Fe_2O_3$ and $Al_2O_3$. Silicate in water has been reported to have no significant effects on adsorption of As(V) by cupric oxide nanoparticles but only slightly inhibited adsorption of As(III) [101]. 1 mg Si/L silicate concentration was reported to increase Arsenic adsorption due to electrostatic effects of $Al_2O_3$ compared to $Fe_2O_3$ adsorbent [60].

*5.1.4. Bicarbonate and Carbonate.* Dissolved carbonate exists as $HCO_3^-$ (bicarbonate) and carbonate ($CO_3^{2-}$) in groundwater and is likely to interfere with arsenic adsorption. Bicarbonate ions are known to form inner-sphere monodentate complexes with surface functional groups of Fe and Al hydroxides. With the existence of 400 mg/L of carbonate concentration in solutions, the percentage of As(III) adsorption decreases to 77%, as it was observed on treated laterite as adsorbents. This was due to the competition between $HCO_3^-$ and $HASO_4^{2-}$ for positively charged adsorption sites [50]. According to Zhang et al. [42], the addition of $CO_3^{2-}$ decreased arsenic adsorption moderately on arsenite and arsenate adsorption by $MnFe_2O_4$ and $CoFe_2O_4$. The decrease of adsorption was due to the basic condition when $Na_2CO_3$ was added and formation of arsenic–carbonate complexes $As(CO_3)^{2-}$, $As(CO_3)(OH)^{2-}$, and $AsCO^{3+}$ in the presence of high concentration of $CO_3^-$ [42].

*5.1.5. Chloride and Nitrate.* Jeong et al. [60] showed that chloride and nitrate anions do not have visible effects on the adsorption of As(V) on $Fe_2O_3$ and $Al_2O_3$ [60]. This was due to the fact that complexes of chloride and nitrate with $Fe_2O_3$ and $Al_2O_3$ are much weaker than those between arsenate and $Al_2O_3$ or $Fe_2O_3$. Similar result was obtained by [61], where nitrate ions were increased from 1 to 10 $mgL^{-1}$ concentrations on the arsenite removal by Fe(VI), Fe(VI)/Fe(III), and Fe(VI)/Al(III) salts, due to lack of competition between $NO_3^-$ and the adsorbent for adsorption sites [61].

*5.2. Effect of Cations.* $Ca^{2+}$ was reported to significantly enhance the adsorption capacity of modified red mud at pH 7.3 [69]. Increasing $Ca^{2+}$ concentration from 0 mg/L to

40 mg/L resulted in an increase of 1 mg/g of arsenate adsorbed. $Ca^{2+}$ was claimed to bond the modified red mud particle with arsenate and form a metal–arsenate complex or metal–$H_2O$–arsenate complex [69]. Effects of $Mg^{2+}$, $Ca^{2+}$, and $Fe^{2+}$ on arsenate As(V) and arsenite AS(III) were studied on nano zerovalent iron on activated carbon, and it was reported that the cations considerably increase the adsorption of arsenate As(V) by increasing the pH [3]. The existence of metal cations in the solution shifted the surface of the adsorbent to more positively charged nature, which on the other hand allowed the adsorbent to show higher affinity for arsenate anions [3]. Meanwhile, $Fe^{2+}$ suppressed arsenite AS(III) adsorption by 4.1% at pH 3.5 and by 22% at pH 6.5 within the presence of $Fe^{2+}$ [3]. The deprotonation of $H_3AsO_3$ at pH < 9 controlled the arsenite adsorption, whereas surface charge was not important. $Fe^{2+}$ ions form complexes with arsenite in aqueous solution, and, as a result, the degree of deprotonation/dissociation is repressed, and the adsorption was reduced [3]. As(III) removal was increased with an increase of $Mg^{2+}$, $Ca^{2+}$, and $Fe^{2+}$ concentration on iron oxide-coated cement (IOCC): the enhancement of As(III) adsorption onto the adsorbent surface was attributed to the formation of a surface species, whereby $Mg^{2+}$, $Ca^{2+}$, and $Fe^{2+}$ ions cause the negative charges to be weak and act as a link between the adsorbent surface and the As(III) ions, as it was reported in the study conducted by Kundu and Gupta [70].

### 5.3. Effect of Organic Matter.

Natural organic matter (NOM), which is a carbon source, comprises the combination of acidic organic molecules, which does not originate from a diversity of natural sources including sediments, water, and soil [126]. NOM concentration in natural waters ranges between 1 and 50 mg/l and may compete with arsenic for sorption sites [127]. The theory was proven by Guan et al. [56] on As(III) removal by $KMnO_4$–Fe(II), whereby, due to the presence of the NOM, the adsorption of other solute decreased by competing for adsorption sites; hence the adsorption sites were reduced [56]. However, it was reported that the NOM adsorption for magnetite nanoparticles is through the interaction of organic functional groups OH and COOH and ligand exchange of surface hydroxyl groups, electrostatic attraction, and hydrogen bonding [127]. NOM has been found to assist in the As(III) oxidation to As (V) under alkaline conditions in the absence of both $O_2$ and light [128]. It was observed that 8 mg/L of NOM reduces the adsorption of arsenic, whereas the adsorption increases with increasing pH in the pH range of 4.0–9.4 [128]. Another study on the adsorption of As(V) on alumina in the presence of fulvic acid (FA) showed that, at a pH between 3 and 7.5, FA reduces As(V) adsorption due to attraction forces and negatively charged surfaces were formed because of the deprotonation of functional groups at pH above pKa. Arsenic removal in the $KMnO_4$–Fe(II) process was reported not to be affected at pH 4, but at pH 5 in 1 mg/L or 4 mg/L humic acid (HA), the adsorption dropped by 9% [56]. Arsenic removal was reported to be decreased by 24.8% at pH of 6 and by 58.4% at pH 7 in the presence of 1 mg/L HA [56].

### 5.4. Effects of Ionic Strength on Arsenic.

The ionic strength has the ability to affect the binding of the adsorbed species [1, 54] and therefore compete for adsorption sites. By determining the effects of ionic strength, the inner-sphere and outer-sphere ion-surface complexes can be distinguished [129]. Outer-sphere complexes are predictable to be more vulnerable to ionic strength variations than inner-sphere complexes because the background electrolyte ions are positioned in the same plane for outer-sphere complexes [1]; therefore a decrease in the adsorption is observed when conversely the electrolyte concentration is increased due to competition for adsorption sites [130]. Ions that form inner-sphere complexes are straight synchronized to surface groups and may not compete or compete at lower percentage with electrolyte ions [130]. Thus, the adsorption is less affected by changing the ionic. In many cases of inner-sphere complex formation, the adsorption increases with increasing electrolyte concentration [130]. This effect is usually attributed to changes in the electric potential in the interface, whereby the electrostatic repulsion between the charged surface and the anion is decreased, and the adsorption is favored [130].

The effect of ionic strength on the As(V) sorption was studied at 0.02 and 0.15 mol $dm^{-3}$ NaCl solutions goethite and jarosite and the result shows that As(V) sorption is independent of ionic strength [92]. The researchers suggested that As(V) adsorption on goethite could proceed via the formation of inner-sphere surface. References [92, 131] studied the effects of ionic strength in magnetite nanoparticles on arsenate and arsenite adsorption, and it was reported that the adsorption decreased by 4% by increasing the ionic strength from 0.01 to 0.1. Guo et al. [99] investigated the effect of background electrolyte (NaCl) concentration on synthetic siderite with 0.001–0.1 mol/L NaCl as background electrolyte. The result showed that As(V) removal was not affected by (NaCl). The increase of ionic strength was reported to increase As(V) adsorption onto $TiO_2$ under alkaline conditions (pH 7.0–11.0). However, under acidic conditions, the adsorption of As(V) onto $TiO_2$ decreased with increasing ionic strength in NaCl electrolyte [126]. Therefore ionic strength is also affected by pH of the solution.

## 6. Fluoride ($F^-$) Adsorption Isotherm and Adsorption Capacity

The adsorption behavior of fluoride by various adsorbents varies depending on the bonding between fluoride species and active sites on the surface of the adsorbent [132]. From the various adsorbents compared (Table 2), the Langmuir and Freundlich equations were the best fit for many adsorbents. The highest adsorption capacity for fluoride removal (400 mg/g) was observed on hydroxyl aluminum oxalate with a surface area of 68.34 $m^2$/g [133] and (600 mg/g) for aluminum fumarate with a surface area of 1156 $m^2$/g [134]. There is no general conclusion on how the type of adsorbent fits the chosen isotherm, since the extent of adsorption depends on many factors including the nature of the adsorbate and adsorbent, surface area, activation of the adsorbent, and experimental conditions. The isotherm may differ on the

TABLE 2: Adsorption isotherm for fluoride ($F^-$) removal.

| Adsorbent | Adsorption capacity mg/g | Surface area $m^2/g$ | Applicable isotherm models | Initial fluoride conc. mg/L | References |
|---|---|---|---|---|---|
| Acidic alumina | 8.4 | 144.27 | Langmuir | 15 | [32] |
| Alkoxide origin alumina | 2 | 100 | Langmuir | 5 | [4] |
| Al(III) modified calcium hydroxyapatite | 32.57 | 258.6 | Langmuir | 10 | [146] |
| Bauxite | 5.16 | 38 | Langmuir | 4–24 | [147] |
| Ceramic | 2.16 | 80.94 | Freundlich and Langmuir | 10 | [40] |
| Chitosan-based mesoporous alumina | 8.264 | 413.65 | Langmuir | 5 | [66] |
| Granular red mud | 0.851 | 10.2 | Redlich–Peterson, Freundlich | 15 | [148] |
| Calcite | 0.39 | 0.057 | Freundlich | $2.5 \times 10^{-5}$ | [149] |
| Quartz | 0.19 | 0.06 | Freundlich | $t0$ | [149] |
| Fluorspar | 1.79 | 0.048 | Freundlich | $6.34 \times 10^{-2}$ | [149] |
| Hydroxyapatite | 4.54 | 0.052 | Freundlich | — | |
| Activated quartz | 1.16 | 0.06 | Freundlich | — | [149] |
| Nano alumina | 14 | 151.7 | Langmuir | — | [29] |
| Magnesia-amended activated alumina granules | 10.12 | 193.5 | Sips (S) | — | [150] |
| Manganese oxide-coated alumina | 2.85 | 170.39 | Langmuir | 2–30 | [151] |
| Mesoporous alumina (meso-Al-400) | 39 | 361 | Langmuir | 10 | [31] |
| Cerium-impregnated fibrous protein | 17.5 | 3.65 | Langmuir | — | [152] |
| Aluminium titanate (AT) | 0.85 | — | Freundlich, Langmuir | 4 | [153] |
| Bismuth aluminate (BA) | 1.55 | — | Freundlich, Langmuir | 4 | [153] |
| Alum-impregnated activated alumina (AIAA) | 40.3 | 176 | Bradley equation | — | [154] |
| Alumina/chitosan (AlCs) composite | 3.809 | 55.23 | Freundlich and Langmuir | — | [155] |
| Alumina cement granules | 4.75 and 3.91 | 4.385 | Langmuir | 20 8.65 | [23] |
| Aluminum hydroxide-coated rice husk ash (AH-coated RHA) | 15 | 50.4 | Freundlich | 10 | [156] |
| Aluminum hydroxide, $Al(OH)_3$ | 25 | 50.4 | Freundlich | 10 | [156] |
| Activated alumina | 2.41 | — | Langmuir | — | [39] |
| Hydrated cement | 2.6788 | — | Freundlich, Langmuir | — | [157] |
| Waste mud | 27.2 | — | Langmuir | 5.0 and 950 | [64] |
| Sol-gel-derived activated alumina, CaO-AA | 96.23 | 255.42 | Langmuir | 0.99 | [135] |
| Sol-gel-derived activated alumina, $MnO_2$-AA | 0.99 | 218.0 | Langmuir | 432 | [135] |
| Aluminum impregnation of activated carbon | 2.549 | — | Langmuir | — | [158] |
| Brushite | 6.59 | — | Langmuir and Freundlich | 25 | [159] |
| Ceramic | 2.16 | 80.94 | Freundlich and Langmuir isotherms | 10 | [40] |
| Granular ceramic | 12.12 | 73.67 | Freundlich | — | [40] |
| Ca650/C charcoal that contains calcium compounds | 19.05 | – | Langmuir | 10 | [160] |

TABLE 2: Continued.

| Adsorbent | Adsorption capacity mg/g | Surface area m$^2$/g | Applicable isotherm models | Initial fluoride conc. mg/L | References |
|---|---|---|---|---|---|
| Titanium dioxide (TiO$_2$) | 0.27 | 56. | Temkin, Dubinin–Radushkevich (DR) | — | [68] |
| Magnetic-chitosan particle | 20.96–23.98 | — | Langmuir, Bradley's | — | [161] |
| Mg–Al–Fe hydrotalcite-like compound | 14 | — | Langmuir | — | [65] |
| Mixed rare earth oxide | 12.5 | 6.75 | Langmuir | 50 | [162] |
| Plaster of Paris | 0.366 | — | Freundlich and Langmuir | 2–10 | [163] |
| Polypyrrole/Fe$_3$O$_4$ magnetic nanocomposite | 17.6–22.3 | — | Freundlich and Langmuir | — | [164] |
| Cross-linked chitosan particles | 8.1 | 4.37 | Freundlich and Langmuir | 11.8 to 59.0 | [165] |
| Carbon derived from *Sargassum* sp. by lanthanum | 94.34 | | Langmuir | | [166] |
| Hydroxyl aluminum oxalate | 400 | | Langmuir | | [133] |
| Hierarchical Ce–Fe bimetal oxides | 60.97 | 164.9 m$^2$/g | Langmuir | | [167] |
| Hydrous ferric oxide doped alginate beads | 8.90 | 25.80 | Langmuir | | [168] |
| Al(III)–Zr(IV) binary oxide | 114.54 mg/g | | Langmuir | | [169] |
| Hierarchical MgO microspheres | 115.5 mg/g | 33.7 | Freundlich model | | [143] |
| Micron-sized magnetic adsorbent (MMA) | 41.8 mg/g | | Langmuir | 200 mg/L | [170] |
| Hydroxyapatite nanowires | 40.65 mg/gat | | | 200 mg/L | [171] |
| Aluminium fumarate | 600 | 1156 m$^2$/g | Freundlich isotherm | 1000 | [134] |

same fluoride concentration according to the type of the adsorbents. For example, [135] reported that Freundlich fitted the sol-gel-derived activated alumina modified with calcium oxide and Langmuir sol-gel-derived activated alumina modified with magnesium oxide.

One of the most widely used adsorbents on fluoride removal is activated alumina and it has widely been applied for fluoride adsorption [22]. However, the adsorption capacity of fluoride on activated alumina depends on pH at large and not on the surface areas of the adsorbent. This can be proven in Figure 4, whereby different adsorbents capacities were compared with their surface area. However, modified activated alumina has shown a considerate higher adsorption capacity compared to unmodified alumina even at high fluoride concentration. For example, [135] reported the removal of fluoride by activated alumina up to 96.23 mg/g for water with a fluoride concentration of 432 mg/L in a sol-gel-derived activated alumina modified with calcium oxide. The reason for the higher adsorption capacity was the alkalinity of the adsorbent and the technique used for modification of the activated alumina. Another study by using sol-gel alumina adsorbents was done on modified immobilized activated alumina (MIAA), and adsorption capacity of 0.76 mg/g was reported compared to 0.47 mg/g for activated charcoal on fluoride concentration of 12 mg/L [136]. Another comparison was made between alkoxide origin alumina and activated alumina on fluoride removal, and higher fluoride uptake

was seen with alkoxide alumina because of Fe$_2$O$_3$ and SiO$_2$, activated carbon pores, and the increased electropositivity of the material [4]. The effectiveness of modified material was also reported by [137] on magnetite modified with aluminum and lanthanum ions for the adsorption of fluoride. The adsorption of fluoride was reported to increase by 60% and 66% for the aluminum and lanthanum modified materials, respectively [137].

Fourier transform infrared (FTIR), scanning electron microscopy (SEM), and Extended X-ray Absorption Fine Structure (EXAFS) spectroscopy are used to clarify the mechanism of fluoride adsorption [133]. Most of the FTIR studies on fluoride removal by different adsorbents have shown the involvement and the participation of the surface sites and potential functional groups in the adsorption, especially the hydroxyl group [138, 139]. It was observed that fluoride interacts with the OH and NH groups on surface aluminum-impregnated coconut fiber surface [140]. However, the adsorption of fluoride on Fe-impregnated chitosan was reported to occur due to ion exchange between fluoride and chloride [141]. Other studies using FTIR have revealed the formation of inner-spherically bonded complexes on $\gamma$−Fe2O3 nanoparticles with fluoride [142]. By using FTIR and XPS analyses, it was concluded that hydroxyl and the surface carbonates participate in the coexchange with fluoride ions on hierarchical magnesium oxide microspheres [143] and on magnesium oxide nanoplates adsorbents [144].
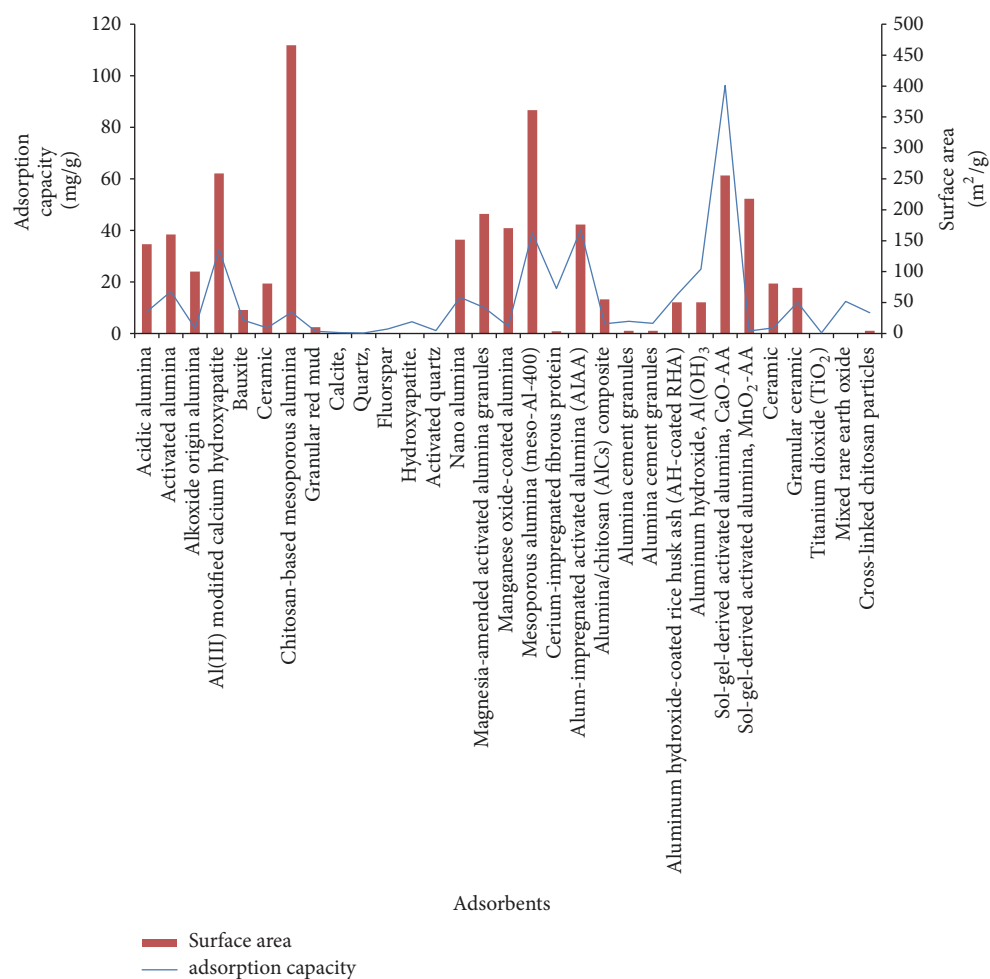
FIGURE 4: Relationship between the adsorption capacity and surface area of the adsorbents for fluoride removal.

Another study revealed that the coexistence of C–O and C=O functional groups on lanthanum-loaded magnetic cationic hydrogel composite contributed to the fluoride adsorption by using FTIR [145].

Both Langmuir and Freundlich isotherm seem to fit well for adsorptions of these anions. However, the choice of the adsorbents to agree with Langmuir or Freundlich is still unclear. Higher adsorption capacity has been observed for fluoride ions compared to arsenic ions. Both modified adsorbents have been shown to have higher adsorption capacity compared to unmodified adsorbents, and, up to date, iron-based adsorbents (IBS) are still suitable material for arsenic adsorption and aluminum for fluoride.

This is the first report to show the relationship between the adsorption capacity and surface area of the adsorbents for arsenic and fluoride removal. It can be concluded that high surface area of the adsorbents does not often cause higher adsorption capacity on these anions' removal but rather the chemical properties of the adsorbents. Modified adsorbents have been proven to be effective for the anions removal because modifications of adsorbents alter the physical and chemical properties of the adsorbents. For example, Gong et al. [132] studied different types of alumina and concluded

that the acidity and basicity properties of the alumina significantly affect the fluoride adsorption and not the surface area.

Chen et al. [172] reported that adsorption of fluoride on $PPy/TiO_2$ was not affected by surface area. $PPy/TiO_2$ has a surface area of $95.71 \, m^2/g$, and its maximum adsorption capacity was $33.178 \, mg/g$ at $25°C$ with an initial fluoride concentration of $11.678 \, mg/L$. The author concluded that physical adsorption was not the primary adsorption mechanism for the adsorption of fluoride on $PPy/TiO_2$. Another study on adsorption of fluoride by a synthetic iron(III)–aluminum(III) mixed oxide with a specific surface area of $195.6 \, m^2/g$ reached a maximum fluoride removal of $17.73 \, mg/g$ [173]. Zhang et al. [170] investigate the fluoride adsorption on micron-sized magnetic $Fe_3O_4@Fe$-Ti composite adsorbent (MMA) with a specific surface area of $99.2 \, m^2/g$ and pore size of $0.38 \, cm^3/g$. The model followed Langmuir in isotherm study, and a high maximum adsorption value of $41.8 \, mg/g$ was observed [170]. Adsorption of fluoride on aluminum-impregnated coconut fiber ash (AICFA) was investigated by Mondal et al. [140]. AICFA has a surface area of $26.3 \, m^2/g$ and $3.192 \, mg/g$ adsorption capacity. Another study reported $40.3 \, mg/g$ fluoride removal from drinking water by adsorption onto

alum-impregnated activated alumina with a surface area of $176 \, \text{m}^2/\text{g}$ [154]. Low adsorption capacity for adsorbents with the higher surface area was also reported. For example, a study on fluoride adsorption into nanoparticle goethite anchored onto graphene oxide (FeOOH + Ac/GO) with $202.60 \, \text{m}^2/\text{g}$ reached a maximum adsorption capacity of $17.65 \, \text{mg/g}$. Meanwhile, a rice spike like akaganeite anchored onto graphene oxide (FeOOH/GO) which has $255.24 \, \text{m}^2/\text{g}$ reached $19.82 \, \text{mg/g}$ maximum adsorption capacity [174]. Another study reported a higher adsorption capacity of $93.84 \, \text{mg/g}$ when the fluoride concentration was $200 \, \text{mg/L}$ on $Al(OH)_3$ nanoparticles modified hydroxyapatite (Al-HAP) nanowires with a surface area of $104.05 \, \text{m}^2/\text{g}$ on fluoride removal [175].

## 7. Effects of pH on Fluoride Removal

The extent of fluoride adsorption is influenced by pH at large [4, 29]. Since the protonated surface is accountable for anions adsorption, the maximum fluoride adsorption for many adsorbents occurs at acidic pH [32, 63] and decreases at higher pH values. For adsorbents like activated alumina, fluoride adsorption is controlled by pH at point zero charges (pHzpc) [32, 73]. At a certain selected pH, the adsorption showed an increasing trend due to the positively charged alumina complexes $AlF^{2+}$ and $AlF_2^+$ on fluoride removal by acidic alumina [32]. The fluoride adsorption decreased after pHzpc because the concentration of protonated surface sites decreases with increasing pH [4, 73], which causes strong competition of hydroxide ions [57]. A similar observation was reported by [66] on defluoridation of drinking water using chitosan-based mesoporous alumina. Nie et al. [146] reported maximum fluoride removal of 75% at pH of 5 and the adsorption decreased further as the pH increases on Al (III) modified calcium hydroxyapatite.

The adsorption of fluoride decreases below or above a certain pH value, as it has been reported by various researchers. For example, Li et al. [31] studied the effect of pH on amorphous alumina supported on carbon nanotubes. The result showed that the maximum fluoride adsorption occurred at pH 5.0–9.0 but decreased at pH less than 3.0 and more than 11.0. However, the distribution of $F^-$ and HF on the surface was reported to be the reason for a decrease of fluoride at pH less than 5 on fluoride removal by aluminum-impregnated coconut fiber [140]. Similar results were reported by Tang et al. [63] on the adsorption of fluoride by granular ferric hydroxide, where at pH below 3, the HF were predominant.

Fluoride adsorption capacity was steady within a pH range of 2–11 on porous MgO nanoplates; however, it decreases abruptly at higher pH value above 12 [31, 144]. Tor et al. [148] also reported similar results in the removal of fluoride from water by using granular red mud (GRM). However, other studies reported maximum fluoride removal at neutral pH [29]. Huang et al. [165] observed that the maximum adsorption capacity by using protonated cross-linked chitosan particles was at pH 7. Moreover, a decrease below pH 7 and above was also observed on iron oxyhydroxide nanoparticles [176]. In acidic conditions, the decrease in

adsorption capacity was caused by weak hydrofluoric acid. A similar observation was made by [177] on magnesium substituted hydroxyapatite absorbent at a pH below 3 by using different adsorbents as it was reported by [151, 154, 159, 161].

pH is the main parameter that affects the adsorption of these anions for both arsenic and fluoride. However, the adsorption of fluoride into various adsorbents has been reported to vary significantly at both high and low pH values due to the pH at point zero charges (pHzpc) which controls the adsorptions of adsorbents like activated alumina in fluoride adsorption and iron-based adsorbents for arsenic adsorption. The adsorption capacity of arsenic has been changed with changes in pH due to the chemical speciation of arsenic. Many adsorbents tend to remove charged species, which is As(V), which can exist at a wide range of pH compared to As(III).

## 8. Effects of Anion, Cation, and Organic Matter on Fluoride Removal

*8.1. Effects of Anions.* Drinking water contaminated with fluoride always exists with other coions like phosphate, bicarbonate, chloride, carbonate, sulfate, and nitrate [40, 62, 63, 65, 66]. In fluoride adsorption, it is expected that the presence of anions in solution would enhance coulombic repulsion forces between the anions and fluoride or would compete with fluoride for the active adsorption sites and therefore fluoride adsorption is reduced or increased [66, 135, 136, 178, 179]. Eskandarpour et al. [180] reported that, in fluoride adsorption, chloride and nitrate ions form outer-sphere complexes and sulfate and phosphate ions form inner-sphere complexes with binding surfaces. However, sulfate ions partially form outer-sphere complexes or inner-sphere complexes [180]. The adsorption of fluoride will increase due to an increase in ionic strength of the solution and weakening of lateral repulsion between adsorbed fluoride ions. For example, Chen et al. [40] investigated the presence of 20–200 mg/L salt solutions of chloride, nitrate, sulfate, carbonate, and phosphate in fluoride adsorption. Fluoride removal slightly increased in the presence of chloride and nitrate ions. The authors concluded that it was due to an increase in the ionic strength of the solution or weakening of lateral repulsion between adsorbed fluoride ions. Fluoride sorption was slightly decreased by sulfate ion due to the high coulombic repulsive forces, which reduce the probability of fluoride interactions with the active sites [40, 179].

Carbonate and phosphate ions showed a most significant effect on fluoride sorption due to the competition for the same active sites with fluoride and the high affinity and capacity for carbonate and phosphate ions [40]. The divalent nature of sulfate ion in solution may influence strong coulombic repulsive forces which lead to lessening fluoride interaction with the active sites. Similar results were reported by [38, 178, 179]. The effects of these anions on fluoride adsorption have also been reported to be different depending on experiment conditions which include pH, the anions concentrations, and the characteristics of the adsorbent. Recently, Zhang et al. [141] reported that the increasing concentrations of sulfate and carbonate to 200 mg/L cause a decrease in the
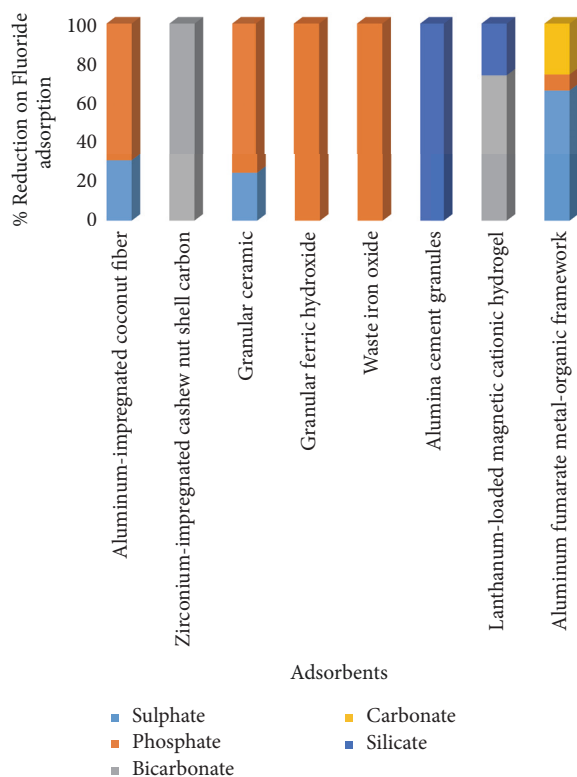
Figure 5: Effects of coexisting anions on fluoride removal on different adsorbents.

fluoride adsorption by 43.24% and 18.77%, respectively, while 100 mg Cl$^-$/L increases the fluoride adsorption capacity of 0.58 mg/g by 2.53 mg/g with 5 mg of HCO$_3$. For the former, the decrease was because of the electrostatic interactions of the anions and the adsorbent, and for the latter, the reaction of bicarbonate with ammonium acetate leads to the decrease of the ammonium acetate concentration.

Other researchers have reported a decrease depending on pH. At pH between 4.4 and 12, 500 mg/L of carbonate and bicarbonate ions concentration was reported to decrease the fluoride adsorption on acidic alumina [32]. Fluoride adsorption was reduced significantly as bicarbonate was acting as a pH buffering agent, and its existence in solution increases and buffered the pH; therefore, the adsorption of fluoride was decresed [4, 155, 166] Kamble et al. [4] reported that the addition of CO$_3$$^{2-}$, SO$_4$$^{2-}$, and HCO$_3$$^-$ ions increases pH of fluoride solution in adsorption of fluoride on alumina of alkoxide nature. Similar results were observed by [29, 147, 165, 181]. Adsorption of fluoride is more affected by the presence of phosphate (Figure 5) compared to other coexisting anions.

Changing of pH to alkaline condition (11.5) was reported to decrease the adsorption capacity of fluoride by more than 25% in the presence of carbonate [134]. The decrease in fluoride adsorption observed by the presence of HCO$_3$$^-$, CO$_3$$^{2-}$, and SO$_4$$^{2-}$ was due to the competition for active sorption sites or due to the change in pH or combination of them [4, 29, 147, 160, 161, 163–167, 181], where the decrease of fluoride was related to anions competitions or effects of pH;

however, in the same study, it was reported that sulfate did not have significant effect on fluoride removal [157]. A similar study was reported on MgO nanoplates [144].

The coexisting anions silicate and phosphate have been reported to have a negligible effect on the fluoride removal on a micron-sized magnetic Fe$_3$O$_4$@Fe-Ti composite adsorbent compared to 160 mg/L SiO$_3$$^{2-}$ and 20 mg/L PO$_4$$^3$ which decreased the adsorption efficiency [170]. Effects of phosphate on fluoride removal were also reported by [146]. The tendency of the anions to form inner-sphere complexes was reported by [28, 29, 32, 63, 170, 174, 175, 177, 178, 180–183]. Chloride ions formed outer-sphere surface complexes and had a minor effect on fluoride adsorption; thus they are less absorbed on the absorbent surface [65]. Anion affinity for a surface site is associated with the physicochemical characteristics of the adsorption mechanism [40, 147, 179]. Another study demonstrated effects of coexisting ions on the removal of fluoride due to changing pH after salt addition and not the competitive adsorption of coexisting ions [184].

*8.2. Effects of Cations.* Only a few studies to date have reported the effects of cations on fluoride removal. At higher cations concentrations, effects become significant. Contradictory results have been presented for cations removal. Some researchers reported increased fluoride adsorption, while others reported a decrease in fluoride adsorption. An increase in adsorption capacity was observed with a higher concentration of magnesium and calcium due to

an increase in surface positive charges and attraction of negatively charged ions onto various metal oxide surfaces on fluoride removal by nano magnesia (NM), as shown in the study conducted by Maliyekkal et al. [62]. Similar effects were observed by [157] at 400 mg/L of $Ca^{2+}$ by using hydrated cement and on alumina cement granules [23]. Also, the formation of insoluble $CaF_2$ and $MgF_2$ was the reason for the increase of adsorption by granular ceramic at 200 mg/L and $Ca^{2+}$ and $Mg^{2+}$ concentration [40]; however, $Mn^{2+}$ and $Fe^{3+}$ at 200 mg/L were reported to decrease fluoride removal capacity up to 10% on nano magnesia [62]. Babaeivelni and Khodadoust [68] reported that the effects of calcium and magnesium ions on fluoride removal onto crystalline titanium dioxide were insignificant.

*8.3. Effects of Organic Matter on Fluoride Adsorption.* Natural organic matter (NOM) molecules consist of combinations of functional groups, including ester, phenolic, amino, nitroso, carboxylic, sulfhydryl, quinone, and hydroxyl, and most of them are negatively charged at neutral pH [23]. Thus NOM can compete with fluoride due to the principal anionic character together with high reactivity on both metals and surfaces [23]. The presence of NOM influences the fluoride adsorption either by decreasing the adsorption or increasing it. Only a few studies have presented the influence of NOM on fluoride adsorption, and the results presented vary at large.

The presence of humic acid was reported to cause a 50% reduction in fluoride removal efficiency by manganese oxide-coated alumina as an adsorbent; this was due to the blocking of active $MnO_2$ sites by the larger humic acid molecule [151]. According to Ayoob and Gupta [23], the adsorption by using alumina cement granules was reduced with increasing NOM concentration because the adsorption capacity was dependent on the availability of the organic molecules and the inner surface of the adsorbent; thus the NOM can access mesopores of the adsorbent and the small molecules can access micropores. However, a study on carbon derived from *Sargassum* sp. by lanthanum indicated that there were insignificant effects on the adsorption of fluoride because the humic acid can be adsorbed on the surface of the activated carbon [166]. Samarghandi et al. [185] reported that, with 20 mg/L of NOM, fluoride adsorption by activated alumina was enhanced at a pH value of 5.5 to 6.

Adsorption of fluoride is more affected by the presence of phosphate compared to other coexisting anions. However, for arsenic adsorption, the influence of phosphate and other existing anions is affected by pH which controls the effects of arsenic to be adsorbed by the adsorbents if they are present in the water. Ionic strength can also interfere with the adsorption of these anions in the presence of other existing anions, and physicochemical characteristics of the adsorption mechanism affect the anion affinity for a surface site. Cations like $Mg^{2+}$, $Ca^{2+}$, and $Fe^{2+}$ have been reported to increase the adsorption of the fluoride and arsenic by using different adsorbents. The presence of NOM influences the fluoride adsorption either by decreasing the adsorption or increasing it. However, pH also affects arsenic adsorption if NOM are

also present by decreasing or increasing the extent of arsenic adsorption into the adsorbents.

*8.4. Effects of Ionic Strength Fluoride.* So far, very few studies have been done on the effects of ionic strength on fluoride removal. However, the importance of ionic strength lies in the fact that it can be used to distinguish whether inner-sphere or outer-sphere surface complexes are formed during the adsorption. It has been related to pH of the solution and characteristics of the adsorbent. Ionic strength has been reported to have insignificant effects on the fluoride removal by micron-sized magnetic $Fe_3O_4@Fe$-Ti composite and was confirmed to form an inner-sphere complex on the surface of the adsorbent [170]. However, the fluoride adsorption was inhibited by the increase of ionic strength, and therefore the adsorption process occurred through the outer-sphere complex adsorption mechanism on fluoride removal by carbon derived from *Sargassum* sp. by lanthanum [166]. Similar results were reported by [73] on fluoride adsorption onto granular ferric hydroxide and [73] on the adsorption of fluoride on activated alumina.

In general, presence of ionic strength can affect the adsorption of both arsenic and fluoride through the formation of inner-sphere or outer-sphere surface complexes. When the adsorption occurs through the inner sphere, there is less competition for adsorption sites; therefore, increasing the salt concentrations increases the adsorption. However, the ionic strength is also affected by pH of the solution when present with arsenic and fluoride anion in water.

# 9. Conclusion

Adsorption of both arsenic and fluoride is largely affected by environmental factors such as pH solution, ionic strength, and coexisting substances such as anions, cations, and organic matter. The adsorption capacity of the adsorbents depends not only on the surface area, pore volume, and particles size but also on a combination of all factors, surface chemistry, and pore structure. Specific area of the adsorbents does not contribute to the adsorption capacity on the removal of these anions from water. Therefore selection of the adsorbents for these anions removal should be based on a combination of all factors for the adsorbents and adsorbate. However, surface modification of the adsorbents increases the adsorption capacity of the adsorbents for removal of these anions due to the presence of more protonated surface sites which favor the removal of these anions. In general, pH has a greater influence on adsorption capacity at large, since it affects the ionic strength and the presence of coexisting anions such as bicarbonate, sulfate, and silica and it affects the surface charges of the adsorbents and the ionic species which can be present in the solution. Modified aluminum adsorbents have shown higher adsorption capacity for fluoride and modified iron oxide and aluminum minerals for arsenic. The adsorption of fluoride and arsenic is inhibited by the presence of phosphate followed by sulfate and silicate. Fourier transform infrared (FTIR) and Extended X-ray Absorption Fine Structure (EXAFS) spectroscopy

have revealed new functional groups on adsorbents surface, which participate in the adsorption of arsenic and fluoride.

## Disclosure

This research did not receive any specific grant from funding agencies in the public or commercial or nonprofit organizations.

## Conflicts of Interest

The authors declare that they have no conflicts of interest.

## References

[1] O. Ajouyed, C. Hurel, M. Ammari, L. B. Allal, and N. Marmier, "Sorption of Cr(VI) onto natural iron and aluminum (oxy)hydroxides: Effects of pH, ionic strength and initial concentration," *Journal of Hazardous Materials*, vol. 174, no. 1-3, pp. 616–622, 2010.

[2] S. M. Maliyekkal, L. Philip, and T. Pradeep, "As(III) removal from drinking water using manganese oxide-coated-alumina: Performance evaluation and mechanistic details of surface binding," *Chemical Engineering Journal*, vol. 153, no. 1-3, pp. 101–107, 2009.

[3] H. Zhu, Y. Jia, X. Wu, and H. Wang, "Removal of arsenic from water by supported nano zero-valent iron on activated carbon," *Journal of Hazardous Materials*, vol. 172, no. 2-3, pp. 1591–1596, 2009.

[4] S. P. Kamble, G. Deshpande, P. P. Barve et al., "Adsorption of fluoride from aqueous solution by alumina of alkoxide nature: Batch and continuous operation," *Desalination*, vol. 264, no. 1-2, pp. 15–23, 2010.

[5] A. Maiti, H. Sharma, J. K. Basu, and S. De, "Modeling of arsenic adsorption kinetics of synthetic and contaminated groundwater on natural laterite," *Journal of Hazardous Materials*, vol. 172, no. 2-3, pp. 928–934, 2009.

[6] B. K. Mandal and K. T. Suzuki, "Arsenic round the world: a review," *Talanta*, vol. 58, no. 1, pp. 201–235, 2002.

[7] USEPA, *Arsenic Occurrence in Public Water Supplies*, epa-815-r-00-023, USEPA, Washington, DC, USA, 2000.

[8] C. Oh, S. Rhee, M. Oh, and J. Park, "Removal characteristics of As(III) and As(V) from acidic aqueous solution by steel making slag," *Journal of Hazardous Materials*, vol. 213-214, pp. 147–155, 2012.

[9] Y. Lee, I.-H. Um, and J. Yoon, "Arsenic (III) oxidation by iron(VI) (ferrate) and subsequent removal of arsenic (V) by iron (III) coagulation," *Environmental Science & Technology*, vol. 37, no. 24, pp. 5750–5756, 2003.

[10] Y. Wu, X. Ma, M. Feng, and M. Liu, "Behavior of chromium and arsenic on activated carbon," *Journal of Hazardous Materials*, vol. 159, no. 2-3, pp. 380–384, 2008.

[11] J. Youngran, M. FAN, J. Van Leeuwen, and J. F. Belcyzk, "Effect of competing solutes on arsenic (V) adsorption using iron and aluminum oxides," *Journal of Environmental Sciences*, vol. 19, no. 8, pp. 910–919, 2007.

[12] M. Chiban, M. Zerbet, G. Carja, and F. Sinan, "Application of low-cost adsorbents for arsenic removal: A review," *Journal of Environmental Chemistry and Ecotoxicology*, vol. 4, no. 5, pp. 91–102, 2012.

[13] C. K. Jain and R. D. Singh, "Technological options for the removal of arsenic with special reference to South East Asia," *Journal of Environmental Management*, vol. 107, no. 1, pp. 1–18, 2012.

[14] S. Mandal, M. K. Sahu, and R. K. Patel, "Adsorption studies of arsenic(III) removal from water by zirconium polyacrylamide hybrid material (ZrPACM-43)," *Water Resources and Industry*, vol. 4, pp. 51–67, 2013.

[15] Y. Glocheux, M. M. Pasarín, A. B. Albadarin, S. J. Allen, and G. M. Walker, "Removal of arsenic from groundwater by adsorption onto an acidified laterite by-product," *Chemical Engineering Journal*, vol. 228, pp. 565–574, 2013.

[16] D. Mohan and C. U. Pittman Jr., "Arsenic removal from water/wastewater using adsorbents—a critical review," *Journal of Hazardous Materials*, vol. 142, no. 1-2, pp. 1–53, 2007.

[17] A. Bhatnagar, E. Kumar, and M. Sillanpää, "Fluoride removal from water by adsorption—a review," *Chemical Engineering Journal*, vol. 171, no. 3, pp. 811–840, 2011.

[18] WHO, Fluoride in drinking-water. WHO/SDE/WSH/03.04/96, 2004.

[19] S. J. Mahmood, N. Taj, F. Parveen, T. H. Usmani, R. Azmat, and F. Uddin, "Arsenic, Fluoride and Nitrate in Drinking Water: The Problem and its Possible Solution," *Research Journal of Environmental Sciences*, vol. 1, no. 4, pp. 179–184, 2007.

[20] Meenakshi and R. C. Maheshwari, "Fluoride in drinking water and its removal," *Journal of Hazardous Materials*, vol. 137, no. 1, pp. 456–463, 2006.

[21] WHO, Fluoride in drinking water. ISBN, 2006, 1900222965.

[22] M. Mohapatra, S. Anand, B. K. Mishra, D. E. Giles, and P. Singh, "Review of fluoride removal from drinking water," *Journal of Environmental Management*, vol. 91, no. 1, pp. 67–77, 2009.

[23] S. Ayoob and A. K. Gupta, "Performance evaluation of alumina cement granules in removing fluoride from natural and synthetic waters," *Chemical Engineering Journal*, vol. 150, no. 2-3, pp. 485–491, 2009.

[24] M. Grassi, G. Kaykioglu, V. Belgiorno, and G. Lofrano, "Removal of Emerging Contaminants from Water and Wastewater by Adsorption Process," in *Emerging Compounds Removal from Wastewater*, SpringerBriefs in Molecular Science, pp. 15–37, Springer Netherlands, Dordrecht, 2012.

[25] A. Dąbrowski, "Adsorption—from theory to practice," *Advances in Colloid and Interface Science*, vol. 93, no. 1–3, pp. 135–224, 2001.

[26] Y. S. Ho, J. F. Porter, and G. McKay, "Equilibrium isotherm studies for the sorption of divalent metal ions onto peat: copper, nickel and lead single component systems," *Water, Air, & Soil Pollution*, vol. 141, no. 1–4, pp. 1–33, 2002.

[27] V. M. C. a. K. J. Vardhan, "Removal of fluoride from water using low cost materials," in *Proceedings of the Fifteenth International Water Technology Conference*, vol. IWTC-15, 2011.

[28] W. Li, C.-Y. Cao, L.-Y. Wu, M.-F. Ge, and W.-G. Song, "Superb fluoride and arsenic removal performance of highly ordered mesoporous aluminas," *Journal of Hazardous Materials*, vol. 198, pp. 143–150, 2011.

[29] E. Kumar, A. Bhatnagar, U. Kumar, and M. Sillanpää, "Defluoridation from aqueous solutions by nano-alumina: Characterization and sorption studies," *Journal of Hazardous Materials*, vol. 186, no. 2-3, pp. 1042–1049, 2011.

[30] F. Di Natale, A. Erto, A. Lancia, and D. Musmarra, "Experimental and modelling analysis of As(V) ions adsorption on granular activated carbon," *Water Research*, vol. 42, no. 8-9, pp. 2007–2016, 2008.

[31] Y.-H. Li, S. Wang, A. Cao et al., "Adsorption of fluoride from water by amorphous alumina supported on carbon nanotubes," *Chemical Physics Letters*, vol. 350, no. 5-6, pp. 412–416, 2001.

[32] A. Goswami and M. K. Purkait, "The defluoridation of water by acidic alumina," *Chemical Engineering Research and Design*, vol. 90, no. 12, pp. 2316–2324, 2012.

[33] S. Chen, Q. Yue, B. Gao, and X. Xu, "Equilibrium and kinetic adsorption study of the adsorptive removal of Cr(VI) using modified wheat residue," *Journal of Colloid and Interface Science*, vol. 349, no. 1, pp. 256–264, 2010.

[34] USEPA, *Technologies and Costs for Removal of Arsenic from Drinking Water*, vol. EPA, 815-R-00-028., USEPA, Washington, DC, USA, 2000.

[35] S. Mor, K. Ravindra, and N. R. Bishnoi, "Adsorption of chromium from aqueous solution by activated alumina and activated charcoal," *Bioresource Technology*, vol. 98, no. 4, pp. 954–957, 2007.

[36] H. Demiral, I. Demiral, F. Tümsek, and B. Karabacakoğlu, "Adsorption of chromium(VI) from aqueous solution by activated carbon derived from olive bagasse and applicability of different adsorption models," *Chemical Engineering Journal*, vol. 144, no. 2, pp. 188–196, 2008.

[37] Y. Li, B. Gao, T. Wu et al., "Hexavalent chromium removal from aqueous solution by adsorption on aluminum magnesium mixed hydroxide," *Water Research*, vol. 43, no. 12, pp. 3067–3075, 2009.

[38] X. Xu, Q. Li, H. Cui et al., "Adsorption of fluoride from aqueous solution on magnesia-loaded fly ash cenospheres," *Desalination*, vol. 272, no. 1–3, pp. 233–239, 2011.

[39] S. Ghorai and K. K. Pant, "Equilibrium, kinetics and breakthrough studies for adsorption of fluoride on activated alumina," *Separation and Purification Technology*, vol. 42, no. 3, pp. 265–271, 2005.

[40] N. Chen, Z. Zhang, C. Feng et al., "An excellent fluoride sorption behavior of ceramic adsorbent," *Journal of Hazardous Materials*, vol. 183, no. 1-3, pp. 460–465, 2010.

[41] K. B. Payne and T. M. Abdel-Fattah, "Adsorption of arsenate and arsenite by iron-treated activated carbon and zeolites: effects of pH, temperature, and ionic strength," *Journal of Environmental Science and Health—Part A: Toxic/Hazardous Substances and Environmental Engineering*, vol. 40, no. 4, pp. 723–749, 2005.

[42] S. Zhang, H. Niu, Y. Cai, X. Zhao, and Y. Shi, "Arsenite and arsenate adsorption on coprecipitated bimetal oxide magnetic nanomaterials: MnFe$_2$O$_4$ and CoFe$_2$O$_4$," *Chemical Engineering Journal*, vol. 158, no. 3, pp. 599–607, 2010.

[43] K. B. Vu, M. D. Kaminski, and L. Nunez, "Review of arsenic removal technologies for contaminated groundwaters.," Tech. Rep. ANL-CMT-03/2, 2003.

[44] W. T. Tsai, C. W. Lai, and K. J. Hsien, "Effect of particle size of activated clay on the adsorption of paraquat from aqueous solution," *Journal of Colloid and Interface Science*, vol. 263, no. 1, pp. 29–34, 2003.

[45] H. Liu, J. Zhang, H. H. Ngo et al., "Effect on physical and chemical characteristics of activated carbon on adsorption of trimethoprim: Mechanisms study," *RSC Advances*, vol. 5, no. 104, pp. 85187–85195, 2015.

[46] S.-J. Park, Y.-S. Jang, J.-W. Shim, and S.-K. Ryu, "Studies on pore structures and surface functional groups of pitch-based activated carbon fibers," *Journal of Colloid and Interface Science*, vol. 260, no. 2, pp. 259–264, 2003.

[47] W. Shen, Z. Li, and Y. Liu, "Surface Chemical Functional Groups Modification of Porous Carbon," *Recent Patents on Chemical Engineering*, vol. 1, no. 1, pp. 27–40, 2010.

[48] V. Tomar and D. Kumar, "A critical study on efficiency of different materials for fluoride removal from aqueous media," *Chemistry Central Journal*, vol. 7, no. 1, article no. 51, 2013.

[49] M. Gallegos-Garcia, K. Ramírez-Muñiz, and S. Song, "Arsenic removal from water by adsorption using iron oxide minerals as adsorbents: A review," *Mineral Processing and Extractive Metallurgy*, vol. 33, no. 5, pp. 301–315, 2012.

[50] A. Maiti, B. K. Thakur, J. K. Basu, and S. De, "Comparison of treated laterite as arsenic adsorbent from different locations and performance of best filter under field conditions," *Journal of Hazardous Materials*, vol. 262, pp. 1176–1186, 2013.

[51] X.-J. Gong, W.-G. Li, D.-Y. Zhang, W.-B. Fan, and X.-R. Zhang, "Adsorption of arsenic from micro-polluted water by an innovative coal-based mesoporous activated carbon in the presence of co-existing ions," *International Biodeterioration & Biodegradation*, vol. 102, pp. 256–264, 2015.

[52] K. Babaeivelni, A. P. Khodadoust, and D. Bogdan, "Adsorption and removal of arsenic (V) using crystalline manganese (II,III) oxide: Kinetics, equilibrium, effect of pH and ionic strength," *Journal of Environmental Science and Health, Part A: Toxic/Hazardous Substances and Environmental Engineering*, vol. 49, no. 13, pp. 1462–1473, 2014.

[53] G. Yang, Y. Liu, and S. Song, "Competitive adsorption of As(V) with co-existing ions on porous hematite in aqueous solutions," *Journal of Environmental Chemical Engineering (JECE)*, vol. 3, no. 3, pp. 1497–1503, 2015.

[54] X. Lv, Y. Hu, J. Tang, T. Sheng, G. Jiang, and X. Xu, "Effects of co-existing ions and natural organic matter on removal of chromium (VI) from aqueous solution by nanoscale zero valent iron (nZVI)-Fe$_3$O$_4$ nanocomposites," *Chemical Engineering Journal*, vol. 218, pp. 55–64, 2013.

[55] A. Afkhami, T. Madrakian, and Z. Karimi, "The effect of acid treatment of carbon cloth on the adsorption of nitrite and nitrate ions," *Journal of Hazardous Materials*, vol. 144, no. 1-2, pp. 427–431, 2007.

[56] X. Guan, H. Dong, J. Ma, and L. Jiang, "Removal of arsenic from water: Effects of competing anions on As(III) removal in KMnO4-Fe(II) process," *Water Research*, vol. 43, no. 15, pp. 3891–3899, 2009.

[57] A. Goswami, P. K. Raul, and M. K. Purkait, "Arsenic adsorption using copper (II) oxide nanoparticles," *Chemical Engineering Research and Design*, vol. 90, no. 9, pp. 1387–1396, 2012.

[58] J. A. Wilkie and J. G. Hering, "Adsorption of arsenic onto hydrous ferric oxide: effects of adsorbate/adsorbent ratios and co-occurring solutes," *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, vol. 107, pp. 97–110, 1996.

[59] A. Maiti, J. K. Basu, and S. De, "Experimental and kinetic modeling of As(V) and As(III) adsorption on treated laterite using synthetic and contaminated groundwater: effects of phosphate, silicate and carbonate ions," *Chemical Engineering Journal*, vol. 191, pp. 1–12, 2012.

[60] Y. Jeong, M. Fan, S. Singh, C.-L. Chuang, B. Saha, and J. Hans van Leeuwen, "Evaluation of iron oxide and aluminum oxide as potential arsenic(V) adsorbents," *Chemical Engineering and Processing: Process Intensification*, vol. 46, no. 10, pp. 1030–1039, 2007.

[61] A. Jain, V. K. Sharma, and O. S. Mbuya, "Removal of arsenite by Fe(VI), Fe(VI)/Fe(III), and Fe(VI)/Al(III) salts: Effect of pH

and anions," *Journal of Hazardous Materials*, vol. 169, no. 1-3, pp. 339–344, 2009.

[62] S. M. Maliyekkal, Anshup, K. R. Antony, and T. Pradeep, "High yield combustion synthesis of nanomagnesia and its application for fluoride removal," *Science of the Total Environment*, vol. 408, no. 10, pp. 2273–2282, 2010.

[63] Y. Tang, X. Guan, J. Wang, N. Gao, M. R. McPhail, and C. C. Chusuei, "Fluoride adsorption onto granular ferric hydroxide: effects of ionic strength, pH, surface loading, and major co-existing anions," *Journal of Hazardous Materials*, vol. 171, no. 1–3, pp. 774–779, 2009.

[64] B. Kemer, D. Ozdes, A. Gundogdu, V. N. Bulut, C. Duran, and M. Soylak, "Removal of fluoride ions from aqueous solution by waste mud," *Journal of Hazardous Materials*, vol. 168, no. 2-3, pp. 888–894, 2009.

[65] W. Ma, N. Zhao, G. Yang, L. Tian, and R. Wang, "Removal of fluoride ions from aqueous solution by the calcination product of Mg-Al-Fe hydrotalcite-like compound," *Desalination*, vol. 268, no. 1-3, pp. 20–26, 2011.

[66] S. Jagtap, M. K. N. Yenkie, N. Labhsetwar, and S. Rayalu, "Defluoridation of drinking water using chitosan based mesoporous alumina," *Microporous and Mesoporous Materials*, vol. 142, no. 2-3, pp. 454–463, 2011.

[67] T. B. Mlilo, L. R. Brunson, and D. A. Sabatini, "Arsenic and fluoride removal using simple materials," *Journal of Environmental Engineering*, vol. 136, no. 4, pp. 391–398, 2010.

[68] K. Babaeivelni and A. P. Khodadoust, "Adsorption of fluoride onto crystalline titanium dioxide: Effect of pH, ionic strength, and co-existing ions," *Journal of Colloid and Interface Science*, vol. 394, no. 1, pp. 419–427, 2013.

[69] S. Zhang, C. Liu, Z. Luan, X. Peng, H. Ren, and J. Wang, "Arsenate removal from aqueous solutions using modified red mud," *Journal of Hazardous Materials*, vol. 152, no. 2, pp. 486–492, 2008.

[70] S. Kundu and A. K. Gupta, "Adsorptive removal of As(III) from aqueous solution using iron oxide coated cement (IOCC): Evaluation of kinetic, equilibrium and thermodynamic models," *Separation and Purification Technology*, vol. 51, no. 2, pp. 165–172, 2006.

[71] S. Gupta and B. V. Babu, "Removal of toxic metal Cr(VI) from aqueous solutions using sawdust as adsorbent: equilibrium, kinetics and regeneration studies," *Chemical Engineering Journal*, vol. 150, no. 2-3, pp. 352–365, 2009.

[72] W. Ding, H. Turson, and X. Huang, "Primary study of fluoride removal from aqueous solution by activated ferric hydroxide," in *Proceedings of the 2nd International Conference on Bioinformatics and Biomedical Engineering, iCBBE 2008*, pp. 2911–2913, China, May 2008.

[73] Y. Tang, X. Guan, T. Su, N. Gao, and J. Wang, "Fluoride adsorption onto activated alumina: modeling the effects of pH and some competing ions," *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, vol. 337, no. 1-3, pp. 33–38, 2009.

[74] N. Öztürk and T. E. Bektaş, "Nitrate removal from aqueous solution by adsorption onto various materials," *Journal of Hazardous Materials*, vol. 112, no. 1-2, pp. 155–162, 2004.

[75] J. C. Saha, K. Dikshit, and M. Bandyopadhyay, "Omparative studies for selection of technologies for arsenic removal from drinking water. UNU Inter, Workshop," in *Proceedings of the UNU Inter, Workshop*, pp. 76–84, Dhaka, Bangladesh, 2001.

[76] Y. Kim, C. Kim, I. Choi, S. Rengaraj, and J. Yi, "Arsenic Removal Using Mesoporous Alumina Prepared via a Templating Method," *Environmental Science & Technology*, vol. 38, no. 3, pp. 924–931, 2004.

[77] R. Singh, S. Singh, P. Parihar, V. P. Singh, and S. M. Prasad, "Arsenic contamination, consequences and remediation techniques: a review," *Ecotoxicology and Environmental Safety*, vol. 112, pp. 247–270, 2015.

[78] A. Sigdel, J. Park, H. Kwak, and P.-K. Park, "Arsenic removal from aqueous solutions by adsorption onto hydrous iron oxide-impregnated alginate beads," *Journal of Industrial and Engineering Chemistry*, 2015.

[79] D. E. Giles, M. Mohapatra, T. B. Issa, S. Anand, and P. Singh, "Iron and aluminium based adsorption strategies for removing arsenic from water," *Journal of Environmental Management*, vol. 92, no. 12, pp. 3011–3022, 2011.

[80] M. Streat, K. Hellgardt, and N. L. R. Newton, "Hydrous ferric oxide as an adsorbent in water treatment: part 2. Adsorption studies," *Process Safety and Environmental Protection*, vol. 86, no. 1, pp. 11–20, 2008.

[81] S. A. Chaudhry, Z. Zaidi, and S. I. Siddiqui, "Isotherm, kinetic and thermodynamics of arsenic adsorption onto Iron-Zirconium Binary Oxide-Coated Sand (IZBOCS): Modelling and process optimization," *Journal of Molecular Liquids*, vol. 229, pp. 230–240, 2017.

[82] T. S. Singh and K. K. Pant, "Equilibrium, kinetics and thermodynamic studies for adsorption of As(III) on activated alumina," *Separation and Purification Technology*, vol. 36, no. 2, pp. 139–147, 2004.

[83] V. M. Boddu, K. Abburi, J. L. Talbott, E. D. Smith, and R. Haasch, "Removal of arsenic (III) and arsenic (V) from aqueous medium using chitosan-coated biosorbent," *Water Research*, vol. 42, no. 3, pp. 633–642, 2008.

[84] M. Islam, P. C. Mishra, and R. Patel, "Arsenate removal from aqueous solution by cellulose-carbonated hydroxyapatite nanocomposites," *Journal of Hazardous Materials*, vol. 189, no. 3, pp. 755–763, 2011.

[85] S. R. Chowdhury and E. K. Yanful, "Arsenic and chromium removal by mixed magnetite-maghemite nanoparticles and the effect of phosphate on removal," *Journal of Environmental Management*, vol. 91, no. 11, pp. 2238–2247, 2010.

[86] A. Ramesh, H. Hasegawa, T. Maki, and K. Ueda, "Adsorption of inorganic and organic arsenic from aqueous solutions by polymeric Al/Fe modified montmorillonite," *Separation and Purification Technology*, vol. 56, no. 1, pp. 90–100, 2007.

[87] T.-F. Lin and J.-K. Wu, "Adsorption of arsenite and arsenate within activated alumina grains: equilibrium and kinetics," *Water Research*, vol. 35, no. 8, pp. 2049–2057, 2001.

[88] O. S. Thirunavukkarasu, T. Viraraghavan, and K. S. Subramanian, "Arsenic removal from drinking water using iron oxide-coated sand," *Water, Air, & Soil Pollution*, vol. 142, no. 1-4, pp. 95–111, 2003.

[89] Y.-H. Xu, T. Nakajima, and A. Ohki, "Adsorption and removal of arsenic(V) from drinking water by aluminum-loaded Shirasu-zeolite," *Journal of Hazardous Materials*, vol. 92, no. 3, pp. 275–287, 2002.

[90] S. S. Tripathy and A. M. Raichur, "Enhanced adsorption capacity of activated alumina by impregnation with alum for removal of As(V) from water," *Chemical Engineering Journal*, vol. 138, no. 1–3, pp. 179–186, 2008.

[91] P. Pillewan, S. Mukherjee, T. Roychowdhury, S. Das, A. Bansiwal, and S. Rayalu, "Removal of As(III) and As(V) from water

by copper oxide incorporated mesoporous alumina," *Journal of Hazardous Materials*, vol. 186, no. 1, pp. 367–375, 2011.

[92] M. P. Asta, J. Cama, M. Martínez, and J. Giménez, "Arsenic removal by goethite and jarosite in acidic conditions and its environmental implications," *Journal of Hazardous Materials*, vol. 171, no. 1-3, pp. 965–972, 2009.

[93] C.-S. Jeon, K. Baek, J.-K. Park, Y.-K. Oh, and S.-D. Lee, "Adsorption characteristics of As(V) on iron-coated zeolite," *Journal of Hazardous Materials*, vol. 163, no. 2-3, pp. 804–808, 2009.

[94] J.-C. Hsu, C.-J. Lin, C.-H. Liao, and S.-T. Chen, "Removal of As(V) and As(III) by reclaimed iron-oxide coated sands," *Journal of Hazardous Materials*, vol. 153, no. 1-2, pp. 817–826, 2008.

[95] T. Tuutijärvi, J. Lu, M. Sillanpää, and G. Chen, "As(V) adsorption on maghemite nanoparticles," *Journal of Hazardous Materials*, vol. 166, no. 2-3, pp. 1415–1420, 2009.

[96] D. Borah, S. Satokawa, S. Kato, and T. Kojima, "Sorption of As(V) from aqueous solution using acid modified carbon black," *Journal of Hazardous Materials*, vol. 162, no. 2-3, pp. 1269–1277, 2009.

[97] L. M. Camacho, R. R. Parra, and S. Deng, "Arsenic removal from groundwater by MnO2-modified natural clinoptilolite zeolite: Effects of pH and initial feed concentration," *Journal of Hazardous Materials*, vol. 189, no. 1-2, pp. 286–293, 2011.

[98] S. Mandal, T. Padhi, and R. K. Patel, "Studies on the removal of arsenic (III) from water by a novel hybrid material," *Journal of Hazardous Materials*, vol. 192, no. 2, pp. 899–908, 2011.

[99] H. Guo, Y. Li, and K. Zhao, "Arsenate removal from aqueous solution using synthetic siderite," *Journal of Hazardous Materials*, vol. 176, no. 1-3, pp. 174–180, 2010.

[100] D. Pokhrel and T. Viraraghavan, "Arsenic removal from aqueous solution by iron oxide-coated fungal biomass: A factorial design analysis," *Water, Air, & Soil Pollution*, vol. 173, no. 1-4, pp. 195–208, 2006.

[101] C. A. Martinson and K. J. Reddy, "Adsorption of arsenic(III) and arsenic(V) by cupric oxide nanoparticles," *Journal of Colloid and Interface Science*, vol. 336, no. 2, pp. 406–411, 2009.

[102] M. Gallegos-Garciaa, K. Ramírez-Muñiza, and S. Songa, "Arsenic removal from water by adsorption using iron oxide minerals as adsorbents: A review," *Mineral Processing & Extractive Metall Rev*, vol. 33, 2012.

[103] Y.-N. Chen, L.-Y. Chai, and Y.-D. Shu, "Study of arsenic(V) adsorption on bone char from aqueous solution," *Journal of Hazardous Materials*, vol. 160, no. 1, pp. 168–172, 2008.

[104] N. Zhu, T. Yan, J. Qiao, and H. Cao, "Adsorption of arsenic, phosphorus and chromium by bismuth impregnated biochar: Adsorption mechanism and depleted adsorbent utilization," *Chemosphere*, vol. 164, pp. 32–40, 2016.

[105] M. R. Yazdani, T. Tuutijärvi, A. Bhatnagar, and R. Vahala, "Adsorptive removal of arsenic(V) from aqueous phase by feldspars: kinetics, mechanism, and thermodynamic aspects of adsorption," *Journal of Molecular Liquids*, vol. 214, pp. 149–156, 2016.

[106] P. Suresh Kumar, R. Q. Flores, C. Sjöstedt, and L. Önnby, "Arsenic adsorption by iron-aluminium hydroxide coated onto macroporous supports: insights from X-ray absorption spectroscopy and comparison with granular ferric hydroxides," *Journal of Hazardous Materials*, vol. 302, pp. 166–174, 2016.

[107] Y. Chen, Y. Zhu, Z. Wang et al., "Application studies of activated carbon derived from rice husks produced by chemical-thermal process - A review," *Advances in Colloid and Interface Science*, vol. 163, no. 1, pp. 39–52, 2011.

[108] A. F. Hassan, A. M. Abdel-Mohsen, and H. Elhadidy, "Adsorption of arsenic by activated carbon, calcium alginate and their composite beads," *International Journal of Biological Macromolecules*, vol. 68, pp. 125–130, 2014.

[109] A. Sherlala, A. Raman, and M. Bello, "Adsorption of arsenic from aqueous solution using magnetic graphene oxide," *IOP Conference Series: Materials Science and Engineering*, vol. 210, p. 012007, 2017.

[110] C. L. Chuang, M. Fan, M. Xu et al., "Adsorption of arsenic(V) by activated carbon prepared from oat hulls," *Chemosphere*, vol. 61, no. 4, pp. 478–483, 2005.

[111] P. Roy, N. K. Mondal, S. Bhattacharya, B. Das, and K. Das, "Removal of arsenic(III) and arsenic(V) on chemically modified low-cost adsorbent: batch and column operations," *Applied Water Science*, vol. 3, no. 1, pp. 293–309, 2013.

[112] B. K. Biswas, J.-I. Inoue, K. Inoue et al., "Adsorptive removal of As(V) and As(III) from water by a Zr(IV)-loaded orange waste gel," *Journal of Hazardous Materials*, vol. 154, no. 1-3, pp. 1066–1074, 2008.

[113] Z. Liu, F.-S. Zhang, and R. Sasai, "Arsenate removal from water using Fe3O4-loaded activated carbon prepared from waste biomass," *Chemical Engineering Journal*, vol. 160, no. 1, pp. 57–62, 2010.

[114] V. K. Sharma and M. Sohn, "Aquatic arsenic: toxicity, speciation, transformations, and remediation," *Environment International*, vol. 35, no. 4, pp. 743–759, 2009.

[115] USEPA, *Arsenic Treatment Technology Evaluation Handbook for Small Systems*, vol. EPA 816-R-03-014, USEPA, Washington,DC, USA, 2003.

[116] S. Kundu and A. K. Gupta, "Sorption kinetics of As(V) with iron-oxide-coated cement - A new adsorbent and its application in the removal of arsenic from real-life groundwater samples," *Journal of Environmental Science and Health, Part A: Toxic/Hazardous Substances and Environmental Engineering*, vol. 40, no. 12, pp. 2227–2246, 2005.

[117] H. Fakour, Y.-F. Pan, and T.-F. Lin, "Effect of humic acid on arsenic adsorption and pore blockage on iron-based adsorbent," *Water, Air, & Soil Pollution*, vol. 226, no. 2, article no. 2224, 2015.

[118] Y. Mamindy-Pajany, C. Hurel, N. Marmier, and M. Roméo, "Arsenic adsorption onto hematite and goethite," *Comptes Rendus Chimie*, vol. 12, no. 8, pp. 876–881, 2009.

[119] P. Lakshmipathiraj, B. R. V. Narasimhan, S. Prabhakar, and G. Bhaskar Raju, "Adsorption of arsenate on synthetic goethite from aqueous solutions," *Journal of Hazardous Materials*, vol. 136, no. 2, pp. 281–287, 2006.

[120] J. Giménez, M. Martínez, J. de Pablo, M. Rovira, and L. Duro, "Arsenic sorption onto natural hematite, magnetite, and goethite," *Journal of Hazardous Materials*, vol. 141, no. 3, pp. 575–580, 2007.

[121] Y. Mamindy-Pajany, C. Hurel, N. Marmier, and M. Roméo, "Arsenic (V) adsorption from aqueous solution onto goethite, hematite, magnetite and zero-valent iron: Effects of pH, concentration and reversibility," *Desalination*, vol. 281, no. 1, pp. 93–99, 2011.

[122] S. Luther, N. Borgfeld, J. Kim, and J. G. Parsons, "Removal of arsenic from aqueous solution: A study of the effects of pH and interfering ions using iron oxide nanomaterials," *Microchemical Journal*, vol. 101, pp. 30–36, 2012.

[123] R. Ansari and M. Sadegh, "Application of activated carbon for removal of arsenic ions from aqueous solutions," *E-Journal of Chemistry*, vol. 4, no. 1, pp. 103–108, 2007.

[124] H. Guo, Y. Li, K. Zhao, Y. Ren, and C. Wei, "Removal of arsenite from water by synthetic siderite: Behaviors and mechanisms," *Journal of Hazardous Materials*, vol. 186, no. 2-3, pp. 1847–1854, 2011.

[125] S. Yao, Z. Liu, and Z. Shi, "Arsenic removal from aqueous solutions by adsorption onto iron oxide/activated carbon magnetic composite," *Journal of Environmental Health Science and Engineering*, vol. 12, no. 1, article no. 58, 2014.

[126] G. J. Liu, X. R. Zhang, L. Mcwilliams, J. W. Talley, and C. R. Neal, "Influence of ionic strength, electrolyte type, and NOM on As(V) adsorption onto TiO2," *Journal of Environmental Science and Health, Part A: Toxic/Hazardous Substances and Environmental Engineering*, vol. 43, no. 4, pp. 430–436, 2008.

[127] S. Yean, L. Cong, C. T. Yavuz et al., "Effect of magnetite particle size on adsorption and desorption of arsenite and arsenate," *Journal of Materials Research*, vol. 20, no. 12, pp. 3255–3264, 2005.

[128] X.-H. Guan, J. Wang, and C. C. Chusuei, "Removal of arsenic from water using granular ferric hydroxide: macroscopic and microscopic studies," *Journal of Hazardous Materials*, vol. 156, no. 1-3, pp. 178–185, 2008.

[129] R. Weerasooriya and H. J. Tobschall, "Mechanistic modeling of chromate adsorption onto goethite," *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, vol. 162, no. 1-3, pp. 167–175, 2000.

[130] J. Antelo, M. Avena, S. Fiol, R. López, and F. Arce, "Effects of pH and ionic strength on the adsorption of phosphate and arsenate at the goethite-water interface," *Journal of Colloid and Interface Science*, vol. 285, no. 2, pp. 476–486, 2005.

[131] H. J. Shipley, S. Yean, A. T. Kan, and M. B. Tomson, "Adsorption of arsenic to magnetite nanoparticles: Effect of particle concentration, pH, ionic strength, and temperature," *Environmental Toxicology and Chemistry*, vol. 28, no. 3, pp. 509–515, 2009.

[132] W.-X. Gong, J.-H. Qu, R.-P. Liu, and H.-C. Lan, "Adsorption of fluoride onto different types of aluminas," *Chemical Engineering Journal*, vol. 189-190, pp. 126–133, 2012.

[133] S. Wu, K. Zhang, J. He et al., "High efficient removal of fluoride from aqueous solution by a novel hydroxyl aluminum oxalate adsorbent," *Journal of Colloid and Interface Science*, vol. 464, pp. 238–245, 2016.

[134] S. karmakar, J. Dechnik, C. Janiak, and S. De, "Aluminium fumarate metal-organic framework: A super adsorbent for fluoride from water," *Journal of Hazardous Materials*, vol. 303, pp. 10–20, 2016.

[135] L. M. Camacho, A. Torres, D. Saha, and S. Deng, "Adsorption equilibrium and kinetics of fluoride on sol-gel-derived activated alumina adsorbents," *Journal of Colloid and Interface Science*, vol. 349, no. 1, pp. 307–313, 2010.

[136] A. Rafique, M. A. Awan, A. Wasti, I. A. Qazi, and M. Arshad, "Removal of fluoride from drinking water using modified immobilized activated alumina," *Journal of Chemistry*, Article ID 386476, 2013.

[137] J. J. García-Sánchez, M. Solache-Ríos, J. M. Martínez-Gutiérrez, N. V. Arteaga-Larios, M. C. Ojeda-Escamilla, and I. Rodríguez-Torres, "Modified natural magnetite with Al and la ions for the adsorption of fluoride ions from aqueous solutions," *Journal of Fluorine Chemistry*, vol. 186, pp. 115–124, 2016.

[138] L. Xu, G. Chen, C. Peng et al., "Adsorptive removal of fluoride from drinking water using porous starch loaded with common metal ions," *Carbohydrate Polymers*, vol. 160, pp. 82–89, 2017.

[139] M. Mohapatra, K. Rout, P. Singh et al., "Fluoride adsorption studies on mixed-phase nano iron oxides prepared by surfactant mediation-precipitation technique," *Journal of Hazardous Materials*, vol. 186, no. 2-3, pp. 1751–1757, 2011.

[140] N. K. Mondal, R. Bhaumik, and J. K. Datta, "Removal of fluoride by aluminum impregnated coconut fiber from synthetic fluoride solution and natural water," *Alexandria Engineering Journal*, vol. 54, no. 4, pp. 1273–1284, 2015.

[141] J. Zhang, N. Chen, Z. Tang, Y. Yu, Q. Hu, and C. Feng, "A study of the mechanism of fluoride adsorption from aqueous solutions onto Fe-impregnated chitosan," *Physical Chemistry Chemical Physics*, vol. 17, no. 18, pp. 12041–12050, 2015.

[142] L. Jayarathna, A. Bandara, W. J. Ng, and R. Weerasooriya, "Fluoride adsorption on $\gamma - fe2o3$ nanoparticles," *Journal of Environmental Health Science and Engineering*, vol. 13, no. 54, 2015.

[143] Z. Jin, Y. Jia, T. Luo et al., "Efficient removal of fluoride by hierarchical MgO microspheres: Performance and mechanism study," *Applied Surface Science*, vol. 357, pp. 1080–1088, 2015.

[144] Z. Jin, Y. Jia, K.-S. Zhang et al., "Effective removal of fluoride by porous MgO nanoplates and its adsorption mechanism," *Journal of Alloys and Compounds*, vol. 675, pp. 292–300, 2016.

[145] S. Dong and Y. Wang, "Characterization and adsorption properties of a lanthanum-loaded magnetic cationic hydrogel composite for fluoride removal," *Water Research*, vol. 88, pp. 852–860, 2016.

[146] Y. Nie, C. Hu, and C. Kong, "Enhanced fluoride adsorption using Al (III) modified calcium hydroxyapatite," *Journal of Hazardous Materials*, vol. 233-234, pp. 194–199, 2012.

[147] M. G. Sujana and S. Anand, "Fluoride removal studies from contaminated ground water by using bauxite," *Desalination*, vol. 267, no. 2-3, pp. 222–227, 2011.

[148] A. Tor, N. Danaoglu, G. Arslan, and Y. Cengeloglu, "Removal of fluoride from water by using granular red mud: batch and column studies," *Journal of Hazardous Materials*, vol. 164, no. 1, pp. 271–278, 2009.

[149] X. Fan, D. J. Parker, and M. D. Smith, "Adsorption kinetics of fluoride on low cost materials," *Water Research*, vol. 37, no. 20, pp. 4929–4937, 2003.

[150] S. M. Maliyekkal, S. Shukla, L. Philip, and I. M. Nambi, "Enhanced fluoride removal from drinking water by magnesia-amended activated alumina granules," *Chemical Engineering Journal*, vol. 140, no. 1-3, pp. 183–192, 2008.

[151] S. M. Maliyekkal, A. K. Sharma, and L. Philip, "Manganese-oxide-coated alumina: A promising sorbent for defluoridation of water," *Water Research*, vol. 40, no. 19, pp. 3497–3506, 2006.

[152] H. Deng and X. Yu, "Adsorption of fluoride, arsenate and phosphate in aqueous solution by cerium impregnated fibrous protein," *Chemical Engineering Journal*, vol. 184, pp. 205–212, 2012.

[153] M. Karthikeyan and K. P. Elango, "Removal of fluoride from water using aluminium containing compounds," *Journal of Environmental Sciences*, vol. 21, no. 11, pp. 1513–1518, 2009.

[154] S. S. Tripathy, J.-L. Bersillon, and K. Gopal, "Removal of fluoride from drinking water by adsorption onto alum-impregnated activated alumina," *Separation and Purification Technology*, vol. 50, no. 3, pp. 310–317, 2006.

[155] N. Viswanathan and S. Meenakshi, "Enriched fluoride sorption using alumina/chitosan composite," *Journal of Hazardous Materials*, vol. 178, no. 1-3, pp. 226–232, 2010.

[156] V. Ganvir and K. Das, "Removal of fluoride from drinking water using aluminum hydroxide coated rice husk ash," *Journal of Hazardous Materials*, vol. 185, no. 2-3, pp. 1287–1294, 2011.

[157] S. Kagne, S. Jagtap, P. Dhawade, S. P. Kamble, S. Devotta, and S. S. Rayalu, "Hydrated cement: A promising adsorbent for the removal of fluoride from aqueous solution," *Journal of Hazardous Materials*, vol. 154, no. 1-3, pp. 88–95, 2008.

[158] R. Leyva Ramos, J. Ovalle-Turrubiartes, and M. A. Sanchez-Castillo, "Adsorption of fluoride from aqueous solution on aluminum-impregnated carbon," *Carbon*, vol. 37, no. 4, pp. 609–617, 1999.

[159] M. Mourabet, H. El Boujaady, A. El Rhilassi et al., "Defluoridation of water using Brushite: Equilibrium, kinetic and thermodynamic studies," *Desalination*, vol. 278, no. 1-3, pp. 1–9, 2011.

[160] E. Tchomgui-Kamga, E. Ngameni, and A. Darchen, "Evaluation of removal efficiency of fluoride from aqueous solution using new charcoals that contain calcium compounds," *Journal of Colloid and Interface Science*, vol. 346, no. 2, pp. 494–499, 2010.

[161] W. Ma, F.-Q. Ya, M. Han, and R. Wang, "Characteristics of equilibrium, kinetics studies for adsorption of fluoride on magnetic-chitosan particle," *Journal of Hazardous Materials*, vol. 143, no. 1-2, pp. 296–302, 2007.

[162] A. M. Raichur and M. J. Basu, "Adsorption of fluoride onto mixed rare earth oxides," *Separation and Purification Technology*, vol. 24, no. 1-2, pp. 121–127, 2001.

[163] V. Gopal and K. P. Elango, "Equilibrium, kinetic and thermodynamic studies of adsorption of fluoride onto plaster of Paris," *Journal of Hazardous Materials*, vol. 141, no. 1, pp. 98–105, 2007.

[164] M. Bhaumik, T. Y. Leswifi, A. Maity, V. V. Srinivasu, and M. S. Onyango, "Removal of fluoride from aqueous solution by Polypyrrole/Fe3O4 magnetic nanocomposite," *Journal of Hazardous Materials*, vol. 186, no. 1, pp. 150–159, 2011.

[165] R. Huang, B. Yang, Q. Liu, and K. Ding, "Removal of fluoride ions from aqueous solutions using protonated cross-linked chitosan particles," *Journal of Fluorine Chemistry*, vol. 141, pp. 29–34, 2012.

[166] Y. Yu, C. Wang, X. Guo, and J. P. Chen, "Modification of carbon derived from *Sargassum* sp. by lanthanum for enhanced adsorption of fluoride," *Journal of Colloid and Interface Science*, vol. 441, pp. 113–120, 2015.

[167] D. Tang and G. Zhang, "Efficient removal of fluoride by hierarchical Ce-Fe bimetal oxides adsorbent: thermodynamics, kinetics and mechanism," *Chemical Engineering Journal*, vol. 283, pp. 721–729, 2016.

[168] M. G. Sujana, A. Mishra, and B. C. Acharya, "Hydrous ferric oxide doped alginate beads for fluoride removal: adsorption kinetics and equilibrium studies," *Applied Surface Science*, vol. 270, pp. 767–776, 2013.

[169] J. Zhu, X. Lin, P. Wu, Q. Zhou, and X. Luo, "Fluoride removal from aqueous solution by Al(III)-Zr(IV) binary oxide adsorbent," *Applied Surface Science*, vol. 357, pp. 91–100, 2015.

[170] C. Zhang, Y. Li, T.-J. Wang, Y. Jiang, and H. Wang, "Adsorption of drinking water fluoride on a micron-sized magnetic Fe3O4@Fe-Ti composite adsorbent," *Applied Surface Science*, vol. 363, pp. 507–515, 2016.

[171] J. He, K. Zhang, S. Wu et al., "Performance of novel hydroxyapatite nanowires in treatment of fluoride contaminated water," *Journal of Hazardous Materials*, vol. 303, pp. 119–130, 2016.

[172] J. Chen, C. Shu, N. Wang, J. Feng, H. Ma, and W. Yan, "Adsorbent synthesis of polypyrrole/TiO2 for effective fluoride removal from aqueous solution for drinking water purification: Adsorbent characterization and adsorption mechanism," *Journal of Colloid and Interface Science*, vol. 495, pp. 44–52, 2017.

[173] K. Biswas, S. K. Saha, and U. C. Ghosh, "Adsorption of fluoride from aqueous solution by a synthetic iron(III)-aluminum(III) mixed oxide," *Industrial & Engineering Chemistry Research*, vol. 46, no. 16, pp. 5346–5356, 2007.

[174] L. Kuang, Y. Liu, D. Fu, and Y. Zhao, "FeOOH-graphene oxide nanocomposites for fluoride removal from water: Acetate mediated nano FeOOH growth and adsorption mechanism," *Journal of Colloid and Interface Science*, vol. 490, pp. 259–269, 2017.

[175] J. He, K. Chen, X. Cai et al., "A biocompatible and novelly-defined Al-HAP adsorption membrane for highly effective removal of fluoride from drinking water," *Journal of Colloid and Interface Science*, vol. 490, pp. 97–107, 2017.

[176] M. Chaudhary, P. Bhattacharya, and A. Maiti, "Synthesis of iron oxyhydroxide nanoparticles and its application for fluoride removal from water," *Journal of Environmental Chemical Engineering (JECE)*, vol. 4, no. 4, pp. 4897–4903, 2016.

[177] P. Garg and C. Chaudhari, "Adsorption of fluoride from drinking water on magnesium substituted hydroxyapatite," in *Proceedings of the 2012 International Conference on Future Environment and Energy IPCBEE*, vol. 28, 2012.

[178] M. S. Onyango, Y. Kojima, O. Aoyi, E. C. Bernardo, and H. Matsuda, "Adsorption equilibrium modeling and solution chemistry dependence of fluoride removal from water by trivalent-cation-exchanged zeolite F-9," *Journal of Colloid and Interface Science*, vol. 279, no. 2, pp. 341–350, 2004.

[179] N. Chen, Z. Zhang, C. Feng, N. Sugiura, M. Li, and R. Chen, "Fluoride removal from water by granular ceramic adsorption," *Journal of Colloid and Interface Science*, vol. 348, no. 2, pp. 579–584, 2010.

[180] A. Eskandarpour, M. S. Onyango, A. Ochieng, and S. Asai, "Removal of fluoride ions from aqueous solution at low pH using schwertmannite," *Journal of Hazardous Materials*, vol. 152, no. 2, pp. 571–579, 2008.

[181] S. S. Tripathy and A. M. Raichur, "Abatement of fluoride from water using manganese dioxide-coated activated alumina," *Journal of Hazardous Materials*, vol. 153, no. 3, pp. 1043–1051, 2008.

[182] A. H. Mahvi, B. Heibati, A. Mesdaghinia, and A. R. Yari, "Fluoride adsorption by pumice from aqueous solutions," *E-Journal of Chemistry*, vol. 9, no. 4, pp. 1843–1853, 2012.

[183] S. Rajkumar, S. Murugesh, V. Sivasankar, A. Darchen, T. Msagati, and T. Chaabane, "Low-cost fluoride adsorbents prepared from a renewable biowaste: Syntheses, characterization and modeling studies," *Arabian Journal of Chemistry*, 2015.

[184] S. Peng, Q. Zeng, Y. Guo, B. Niu, X. Zhang, and S. Hong, "Defluoridation from aqueous solution by chitosan modified natural zeolite," *Journal of Chemical Technology and Biotechnology*, vol. 88, no. 9, pp. 1707–1714, 2013.

[185] M. R. Samarghandi, M. Khiadani, M. Foroughi, and H. Zolghadr Nasab, "Defluoridation of water using activated alumina in presence of natural organic matter via response surface methodology," *Environmental Science and Pollution Research*, vol. 23, no. 1, pp. 887–897, 2016.