



Cite this: *RSC Adv.*, 2022, 12, 32197

# Recent advances of magnetite nanomaterials to remove arsenic from water

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Pure water is one of the major requirements for living beings but water bodies are contaminated with toxic pollutants and heavy metals. Around 225–500 million people on the earth depend on groundwater, which is highly contaminated by arsenic. Arsenic impurities are present in water as arsenite As(III) and arsenate As(V). Arsenic is a highly toxic metalloid ranking one in toxicity. Researchers have been exploring new techniques and methods to purify water. Magnetic nanoparticles have high absorption and reaction capabilities due to their high surface-to-volume ratio and quantum size effects. Due to their high magnetization, adsorption behaviour, and biodegradability, magnetite nanomaterials are considered excellent materials to purify water. These nanomaterials and their composites are cost-effective as well as they can be easily separated, regenerated, and reused. This review gives a recent overview of the potential of magnetite nanoparticles and their composites to treat contaminated water and remove unwanted arsenic impurities.

Received 15th September 2022  
Accepted 27th October 2022

DOI: 10.1039/d2ra05832d

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## 1 Introduction

### 1.1 Contamination of water

Despite more than 70% of the earth being covered with water, available safe drinking water is only 0.3%. Growth in population, rise of industries, and deforestation are the major reasons for clean water scarcity and water contamination. There is a water crisis in the world, and people in many parts of the world do not even get clean water for drinking. This situation would become more complicated in the future due to the increase in the population if the necessary measures are not taken.<sup>1,2</sup> This contaminated water is dangerous for humans, living organisms, and sea creatures. Heavy metals, pharmaceuticals, dyes, pesticides, fertilizers, radioactive elements, *etc.*, could contaminate water to a large extent.<sup>3</sup> Metalloids and heavy metals such as As, Hg, Cd, Cr, and Pb are very dangerous due to their toxicity and non-biodegradability and can cause serious effects on the cardiovascular, gastrointestinal, renal, and nervous systems.<sup>4–6</sup> Out of these metal ions, arsenic has the maximum unfavourable effects on the health of humans because of being more accessible in groundwater than any other metal.<sup>7,8</sup>

### 1.2 Arsenic contamination and its origins

Around 40% of the population of the earth depends on groundwater but groundwater is highly contaminated by arsenic. Arsenic is a highly toxic metal ranking one in toxicity and the 12th most common element that exists on the earth. It is present at low levels in rocks and sediments around the

world.<sup>9</sup> Its presence in water depends on biological activity, weathering reactions, volcanic emissions, and anthropogenic sources. Arsenic originates artificially from oil refineries, chemicals from agriculture, ceramic industries, mineral waste, *etc.*, whereas naturally, it originates from the formation of geological minerals and deposits as depicted in Fig. 1.<sup>10</sup> Arsenic impurities are present in water as arsenite As(III) and arsenate As(V), whereas As(III) is exceedingly toxic compared to As(V).<sup>11</sup>

### 1.3 Effects of arsenic on plants, humans, and animals

Arsenic can contaminate water to a great extent. Excess arsenic concentration in drinking water can lead to skin,

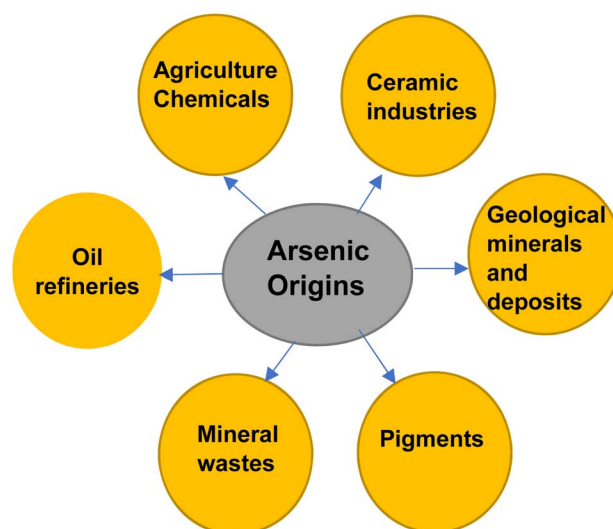


Fig. 1 Origin of arsenic contamination in water.

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cardiovascular, neurological, and respiratory diseases. Its exposure can also cause skin, lung, liver, bladder, and kidney cancer.<sup>12–14</sup> Not only humans, arsenic contamination in water affects animals and plants to a great extent. The main effects of arsenic on plants, humans, and animals are depicted in Fig. 2.<sup>15</sup> Arsenic is mainly found as As(v) and As(III). Surface water has As(v), whereas groundwater has As(III) in the major form; the United States Environmental Protection Agency and the World Health Organization (WHO) have adopted a maximum contamination level of arsenic of  $10 \mu\text{g L}^{-1}$  in drinking water.<sup>16</sup>

#### 1.4 Techniques to remove arsenic from wastewater

People have used various traditional methods to clean water from ancient times. These treatment methods consist of boiling, cloth filtration, storing water in copper vessels, storage for an extended time, solar radiation, *etc.* However, these methods are unsuccessful in the treatment of dissolved pollutants.<sup>17</sup> Different technologies such as ion exchange,<sup>18,19</sup> co-precipitation,<sup>20</sup> reverse osmosis,<sup>21</sup> coal combustion,<sup>22</sup> green methods,<sup>23,24</sup> electrocoagulation,<sup>25</sup> electrodeionization,<sup>26</sup> and membrane filtration<sup>27</sup> are used to remove arsenic from water but these techniques have lower removal efficiencies, produce large amounts of waste, are expensive and produce iron residues.<sup>28</sup> Adsorption is an effective technique to clean water and remove unwanted impurities from water.<sup>29</sup> Adsorption processes are broadly used to clean groundwater and wastewater for drinking and industrial purposes. This method has many advantages for water purification, such as cost-effectiveness, ease of use, flexibility, adaptable design, less energy consumption, *etc.*<sup>30</sup> However, the viability of adsorption processes highly depends on the type of adsorbent, liquid, pollutants, working conditions, process, regeneration, and disposal of waste.<sup>31</sup> The removal efficiency of the adsorbent

highly depends on contact time, pH, adsorbent dosage, and concentration of impurities.<sup>32</sup>

#### 1.5 Nanomaterials for removing arsenic from wastewater

Recently, nanoscale materials are feasible and chemically and ecologically stable having enormously high removal efficiencies and faster kinetics.<sup>33</sup> The properties of the nanoparticles strongly depend on the size of the nanoparticles. It has been reported that nanoparticles having sizes less than 30 nm have a large surface-to-volume ratio and superparamagnetic properties.<sup>34</sup> These nanoparticles lose their magnetization after the removal of the magnetic field, therefore ideal materials for novel separation processes.<sup>35</sup> Nanoparticles have high absorption and reaction capabilities due to their high surface-to-volume ratio and quantum size effects.<sup>36</sup> When the surface area is larger, the reaction would be faster as a large surface area makes more sites available for the reaction for a similar volume, leading to more chemical reactivity.<sup>37</sup> The large surface area of nanoparticles and quantum size effects enhance the reactivity of nanoparticles with contaminants and give a high reaction rate for absorption and separation of pollutants from water.<sup>38</sup>

#### 1.6 Magnetite nanomaterials for water treatment

Magnetic nanomaterials are widely used in water treatment due to the ease of separation and reusability of these materials.<sup>39</sup> Magnetite nanoparticles are extensively used in many applications in the fields of magnetics, electronics, biomedical sciences, and as sensors.<sup>40–43</sup> Magnetite nanoparticles are used as adsorbents in water treatment as they can be separated easily due to high magnetism. These particles could separate and remove the contaminants with the application of external magnetic fields or by centrifugation and filtration.<sup>44</sup> Surface

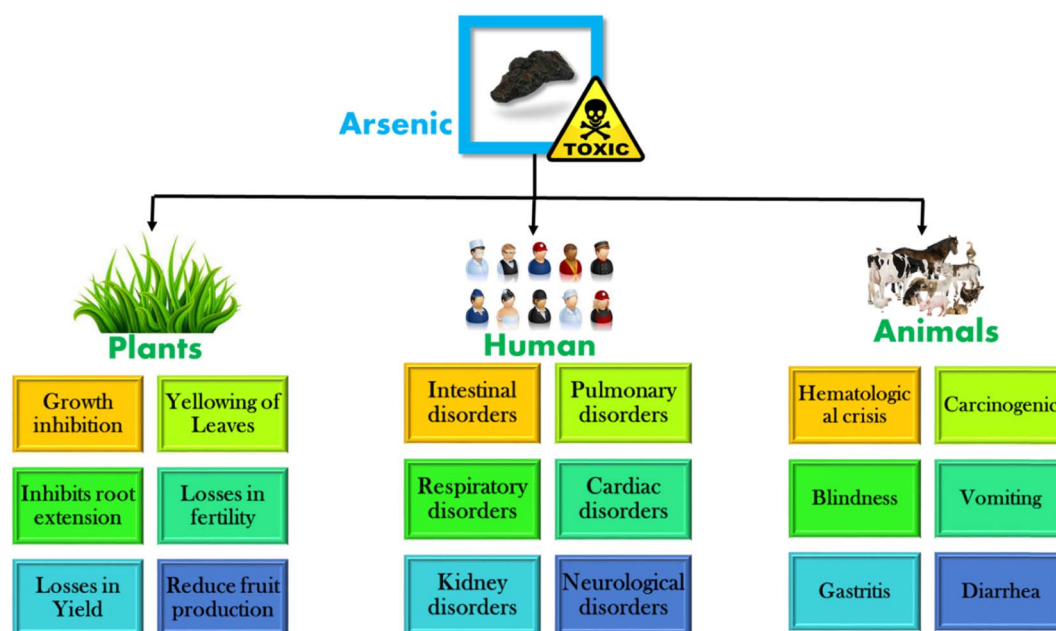


Fig. 2 Effects of arsenic on plants, humans, and animals. Reproduced from ref. 15 with permission from Elsevier, copyright 2021.



modification of these nanoparticles should be required as bare magnetite nanoparticles oxidize easily and aggregate. Also, ferrite nanoparticles show poor stability; therefore, functionalized magnetite composites are widely used for the separation of metals from water and water purification.<sup>45</sup> Therefore, magnetite silica nanocomposites,<sup>46</sup> magnetite-graphene nanocomposites,<sup>47</sup> chitosan-magnetite nanocomposites,<sup>48</sup> magnetite nanoparticle coated sand,<sup>49</sup> *etc.* are widely explored for water purification with enhanced results and cost-effectiveness. In composite nanoparticles, the requirement of large doses gets reduced and the efficiency of functionalized particles enhances.

Many researchers address this worldwide problem of arsenic contamination in various review articles. In these reviews, research focuses on the removal of arsenic contamination using chemically modified natural materials,<sup>50</sup> pressure-driven and thermally driven membranes,<sup>51</sup> a green process using guava leaf biomass, mango bark, and bagasse<sup>52</sup>, electrocoagulation treatment,<sup>53</sup> nano-composites<sup>54</sup> and nanomaterials,<sup>55</sup> layered double hydroxide,<sup>56</sup> hydrotalcite,<sup>57</sup> coal fly ash-based adsorbents,<sup>58</sup> *etc.* In recent years, magnetite nanoparticles and their composites have been widely used for arsenic removal. However, the review of magnetite nanoparticles for the removal of arsenic from water remains unexplored. This review gives a recent overview of the potential of magnetite nanoparticles and their composites to treat contaminated water and remove arsenic from wastewater.

## 2 Adsorption mechanism

### 2.1 Adsorption process using magnetite nanomaterials

Adsorption is a type of interaction between the adsorbent and adsorbate. The solute which is to be removed in the adsorption process is called an adsorbate, while the solid on which it is retained is known as an adsorbent.<sup>59</sup> Several advantages have been cited regarding the adsorption operation. The adsorption process has many advantages; such as, it requires less energy and is cost-effective as many adsorbents can be restored and reused many times. Adsorption is efficient since it can remove or recover all the adsorbate from the solution, providing a perfect separation.<sup>60</sup> Adsorption occurs when the adsorbate in a liquid binds itself to a solid substance's surface. Adsorbents should have a very high internal surface area to ease the adsorption. Arsenic contamination could be removed using

magnetite nanocomposites. These nanocomposites are added to contaminated water and arsenic gets diffused on the nanocomposites. With a suitable magnet's help, these nanocomposites and arsenic could be removed. It was found that arsenic can be bounded by magnetite nanoparticles. A suitable magnetic field could remove this arsenic-magnetite waste effectively, thereby purifying water. For practical use as an adsorbent, the number of reuse cycles and the material's regeneration are vital for enhancing the adsorption process and reducing operational costs. This process could be repeated many times to get clean water as shown in Fig. 3.

Magnetite can be synthesized either by merging atoms/molecules/clusters or breaking down the bulk material into smaller dimensions. These methods are known as the 'bottom up' and 'top down' approaches, respectively,<sup>61–64</sup> as shown in Fig. 4.

Functionalized magnetite composites having a high surface area have been used for such applications. Then their structure, microstructure and magnetic properties were studied performing different techniques including XRD, SEM/EDX, IR, TGA/DSC, TEM, and SQUID magnetometry.

### 2.2 Adsorption models

The amount of material adsorbed can be calculated using the relation<sup>65</sup>

$$q_e = \frac{(C_0 - C_e)V}{m} \quad (1)$$

where  $C_0$  and  $C_e$  are the initial and final concentrations of arsenic in solution ( $\text{mg L}^{-1}$ ),  $V$  is the volume of solution (L) and  $m$  is the mass of the adsorbent (magnetite composite) (g).

Pseudo-first-order and pseudo-second-order kinetics models are used for estimation of adsorption of arsenic for these experimental data and rate controlling steps are fitted in these models (eqn (2) and (3)).<sup>66</sup>

$$\log(q_e - q_t) = \log(q_e) - \frac{k_{\text{ads}}}{2.303} t \quad (2)$$

$$\frac{t}{q_t} = \frac{1}{h} + \frac{t}{q_e} \quad (3)$$

and

$$h = kq_e^2 \quad (4)$$

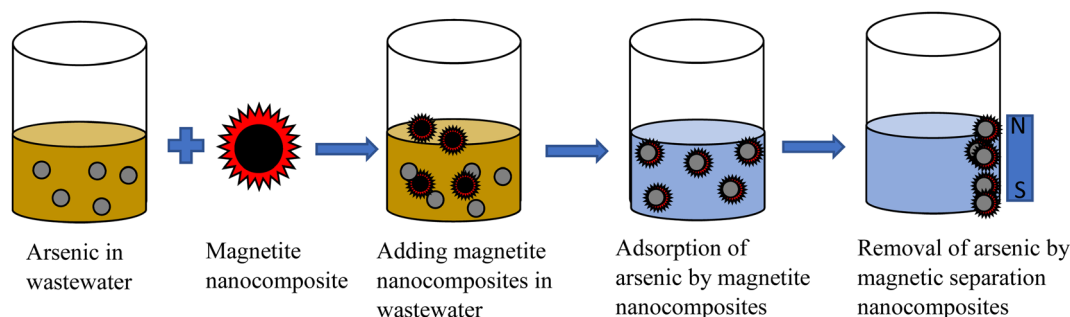


Fig. 3 Process of arsenic removal from wastewater using magnetite nanocomposites.



where  $q_e$  and  $q_t$  are the amounts of absorbed arsenic per unit mass of adsorbent at equilibrium and time  $t$ , respectively, in  $\text{mg g}^{-1}$ . The  $k_{\text{ads}}$  and  $k$  are pseudo-first-order and pseudo-second-order adsorption rate constants, and  $h$  is the initial adsorption rate ( $\text{mg g}^{-1} \text{min}^{-1}$ ).

Freundlich and Langmuir isotherm models can be used to compare experimental adsorption isotherm data. Eqn (5) represents the linear form of the Freundlich isotherm model (Freundlich 1906):<sup>67</sup>

$$\log(q_e) = \log K_F + \frac{1}{n} \log(C_e) \quad (5)$$

$C_e$  is the equilibrium concentration of As(v) in  $\text{mg L}^{-1}$ ,  $K_F$  is the adsorption capacity indicator, and  $n$  ( $1 < n < 10$ ) is the adsorption intensity. Adsorption is considered good if  $n = 1-2$ , better if  $n = 2-10$  and unfavourable if  $n < 1$ .

The Langmuir isotherm model is given by eqn (6) in the linear form as<sup>68</sup>

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + b q_m \quad (6)$$

where  $q_m$  is the maximum adsorption capacity, and  $b$  ( $\text{L mg}^{-1}$ ) is the Langmuir adsorption constant which depends on the force between the solute and adsorbent.

The adsorption efficiency of the process also depends on ' $r$ ' which is a dimensionless quantity calculated by using the relation<sup>68</sup>

$$r = \frac{1}{1 + b C_0} \quad (7)$$

where  $C_0$  is the initial concentration of As(v) and  $b$  is the Langmuir constant.  $r < 1.0$  indicates favorable adsorption, while  $r > 1.0$  shows unfavourable adsorption.

### 3 Arsenic removal using magnetite nano adsorbents

In recent years, iron oxide nanoparticles have exhibited excellent properties in sorption activities due to their high specific surface area, porosity structure, and strong magnetic response, resulting in an exceptional sorption capacity.<sup>69,70</sup>

Magnetic nanomaterials are promising adsorbents because of the directional movement of these nanomaterials in the applied magnetic field. These nanomaterials are widely used to treat wastewater by removing heavy metals due to their exceptional physical and chemical properties such as strong adsorption, superparamagnetic nature, high surface area, biodegradability, non-toxicity, *etc.*<sup>71,72</sup>

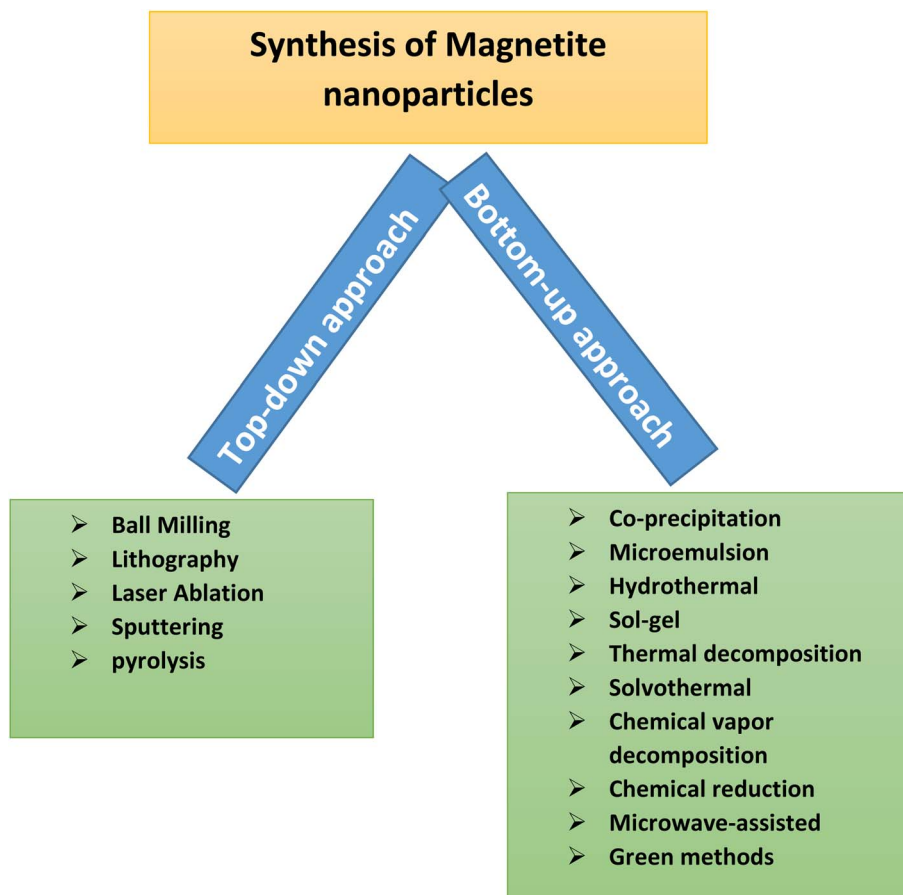
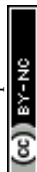


Fig. 4 Techniques to synthesize magnetite nanoparticles.





### 3.1 Magnetite nanomaterials to remove heavy metals and dyes from wastewater

Today's  $\text{Fe}_3\text{O}_4$  nanomaterials are the most preferred magnetic materials for various applications due to their high magnetization, superparamagnetic nature, low Curie temperature, non-toxicity, *etc.* These nanomaterials have shown excellent suitability for water treatment because of their stability, low cost, and regeneration after use.<sup>73,74</sup>

Carboxymethyl cellulose immobilized  $\text{Fe}_3\text{O}_4$  nanoparticles were able to adsorb  $\text{Pb(II)}$  from wastewater.<sup>75</sup> The L-arginine modified magnetic bio adsorbent ( $\text{Fe}_3\text{O}_4\text{-CS-L}$ ) adsorbs  $\text{Zn}^{2+}$ ,  $\text{Cd}^{2+}$ , and  $\text{Pb}^{2+}$  from an aqueous solution by the adsorption method with good recyclability.<sup>76</sup> Surfactant modified magnetite nanoparticles effectively adsorb  $\text{Cd}^{2+}$ ,  $\text{Pb}^{2+}$  and  $\text{Zn}^{2+}$  from wastewater.<sup>77</sup> Iron oxide magnetic nanoparticles (MNPs) grafted on a hyperbranched polyglycerol (HPG) polymer were able to adsorb Ni, Cu, and Al successfully from industrial wastewater.<sup>78</sup> Magnetite nanoparticles loaded on activated carbon ( $\text{Fe}_3\text{O}_4\text{-MNPs-AC}$ ) have shown a high adsorption capacity for dyes from wastewater in a short time.<sup>79</sup> Magnetite nanoparticles exhibited remarkable adsorption for  $\text{Pb}^{2+}$  and  $\text{Cr}^{6+}$ . Mechanisms for  $\text{Pb}^{2+}$  adsorption by magnetite nanoparticles are shown in Fig. 5.<sup>80</sup>

L-Cysteine functionalized magnetite nanoparticles have successfully adsorbed  $\text{Pb}^{2+}$  and  $\text{Cr}^{6+}$  from wastewater and shown good stability and reusability of the adsorbent.<sup>81</sup>

$\text{Fe}_3\text{O}_4@\text{SiO}_2$  core/shell magnetic nanoparticles functionalized with hydrous lanthanum oxide easily adsorb phosphate from water.<sup>82</sup> Magnetite/carbon composites are synthesized using waste fruit peels. These composites could adsorb methyl blue, Congo red, rhodamine B, and  $\text{Cr}^{6+}$  ions for the treatment of wastewater.<sup>83</sup> Composites of magnetite nanoparticles, chitosan nanoparticles, and polythiophene are very efficient in adsorbing Hg from wastewater.<sup>84</sup> Magnetite graphene oxide encapsulated in alginate beads has shown improved performance to adsorb As(v) and Cr(vi) from aqueous solutions.<sup>85</sup> Spent tea-supported magnetite (ST/Mag) nanoparticles successfully removed Cr(vi) from saline wastewater.<sup>86</sup>

### 3.2 Magnetite nanocomposites for arsenic removal from wastewater

**3.2.1 Magnetite-silica nanocomposite.** Porous silica has been used as a carrier vehicle due to the high surface area of these particles which could have applications such as drug delivery agents, catalysis, clean water, *etc.* The high surface area led to the adsorption of unwanted ions rather than bare particles. The adsorption of arsenic increases with increasing its concentrations for both magnetite and magnetite-silica nanocomposite but the adsorption capacity of the magnetite-silica nanocomposite is higher than that of plain magnetite nanoparticles.<sup>46</sup>

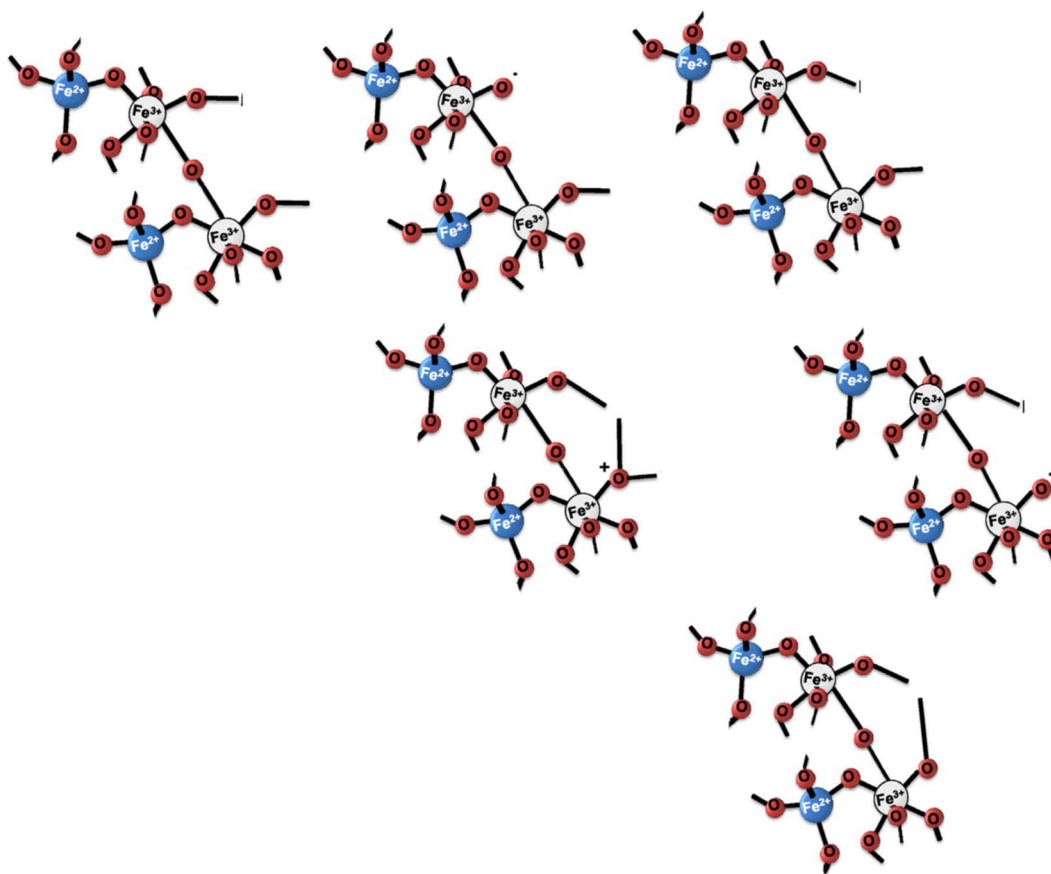


Fig. 5 Lead(II) adsorption on magnetite surfaces. Reproduced from ref. 80 with permission from Elsevier, copyright 2016.

The removal process of arsenic is divided into fast and slow adsorption process rates. It took 30 initial minutes to adsorb 87% of As(v) using magnetite nanoparticle coated sand as the adsorbent, while in the next 330 min, the removal efficiency increased to 99.84% and As(v) concentration was reduced below  $5 \mu\text{g L}^{-1}$  from  $6700 \mu\text{g L}^{-1}$ . It was observed that magnetite nanoparticle coated sand could adsorb As(v) more effectively in the acidic pH range (2–7) rather than the basic pH range (7–12). As(v) removal efficiency decreased from 99.99 to 39.33% with increasing pH from 7 to 12.<sup>87</sup>

**3.2.2 Magnetite–graphene nanocomposites.** Graphene-based materials were observed to be good adsorbents.<sup>88</sup> Due to the cost-ineffectiveness of these particles, these materials could not be used in the treatment of wastewater. However, magnetite–graphene nanocomposites have shown outstanding adsorbing properties and have the potential to be used as a better adsorbent to clean water effectively.<sup>89</sup> pH values play an important role in adsorption. The change in pH could alter the surface charge which subsequently changes the active sites present on the adsorbent material. Researchers found that arsenic removal greatly depends on the pH, ions employed, the size and surface area of nanoparticles, etc.<sup>90</sup>

Non-oxidative graphene (M-nOG) synthesized using a physical exfoliation method showed higher efficiency for arsenic removal. The adsorption of As(v) was maximum at a pH of 4 and decreased sharply with increasing the pH, whereas for As(III), the adsorption capacity was maximum at a pH of 7 as shown in Fig. 6. The adsorption of As(v) on MnGO decreases with increasing the pH due to an increase of the negatively charged surface sites ( $\text{OH}^-$ ) on the adsorbent. These negative charges on the surface of the adsorbent increase, resulting in an increase in repulsion between M-nOG and arsenic.<sup>91</sup> As(III) and As(v) removal is maximum at a temperature of  $35^\circ\text{C}$  as shown in Fig. 6. The decrease in arsenic removal efficiency indicates the exothermic nature of the adsorption process for temperatures above  $35^\circ\text{C}$ . Maximum adsorption capacities observed for As(III) and As(v) were  $32.7 \text{ mg g}^{-1}$  and  $13.1 \text{ mg g}^{-1}$ , respectively. It was observed that the M-nOG could be regenerated even after being reused for five cycles.<sup>16</sup>

It was observed that the adsorption capacity of the magnetite–graphene oxide composite for As(III) and As(v) was  $85 \text{ mg g}^{-1}$  and  $38 \text{ mg g}^{-1}$ , whereas that for the magnetite-reduced graphene oxide composite was  $57 \text{ mg g}^{-1}$  and  $12 \text{ mg g}^{-1}$  for As(III) and As(v). These results showed that an increased amount of magnetite caused significantly higher absorption of arsenic more effectively.<sup>92</sup>

**3.2.3 Magnetic  $\text{Fe}_3\text{O}_4$ /douglas fir biochar composites.** Biochar is a carbonous stable solid resulting from the thermal disintegration of biomass under a low-oxygen atmosphere and could be used as an adsorbent due to its high porosity, surface area, and functionality.<sup>93</sup> Magnetic biochar can separate heavy metals from contaminated water easily.<sup>94</sup> Magnetic  $\text{Fe}_3\text{O}_4$ /douglas fir biochar composites (MBC) were used to convert As(III) into less toxic As(v) via redox reactions. Maximum removal percentages depend on the initial concentrations of As(III). A decrease in removal percentage was found with an increase in initial concentrations of As. Experimental data were fitted in accordance with the Sips, Langmuir, and Freundlich models. For low arsenic concentrations, the Sips model reduces to the Freundlich isotherm, whereas for high concentrations, it follows the character of the Langmuir isotherm. Adsorption vs. time for initial As(III) concentrations and Sips, Langmuir, and Freundlich curves are shown in Fig. 7.<sup>95</sup>

**3.2.4 Magnetite nanocomposites using organic materials.** Superparamagnetic iron oxide nanoparticles were synthesized using tea residue (MION-tea). The adsorption data obeyed the Langmuir equation with a high adsorption capacity of  $188.69 \text{ mg g}^{-1}$  for arsenic(III), and  $153.8 \text{ mg g}^{-1}$  for arsenic(v). The maximum removal (56.4% to 98.4%) of As(III) occurs with an increase in adsorbent dose from  $0.01$  to  $0.25 \text{ g L}^{-1}$ , followed by no change in removal percentage due to the starting equilibrium condition. The removal percentage of arsenic highly depends on the initial amount, the concentration of As(III) and the pH of the solution as shown in Fig. 8. The number of active sites on the adsorbent surface is not sufficient to adsorb As(III) ions at higher concentrations but at low concentration, the ratio of surface active sites to total As(II) is large, and hence As(III) ions

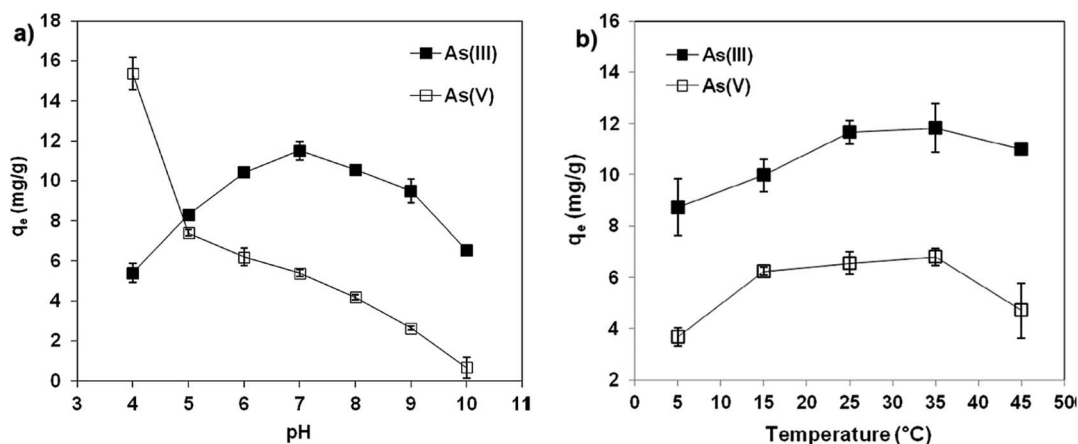


Fig. 6 Effect of (a) pH and (b) temperature on As(III) and As(v) adsorption by M-nOG. Reproduced from ref. 16 with permission from Elsevier, copyright 2017.



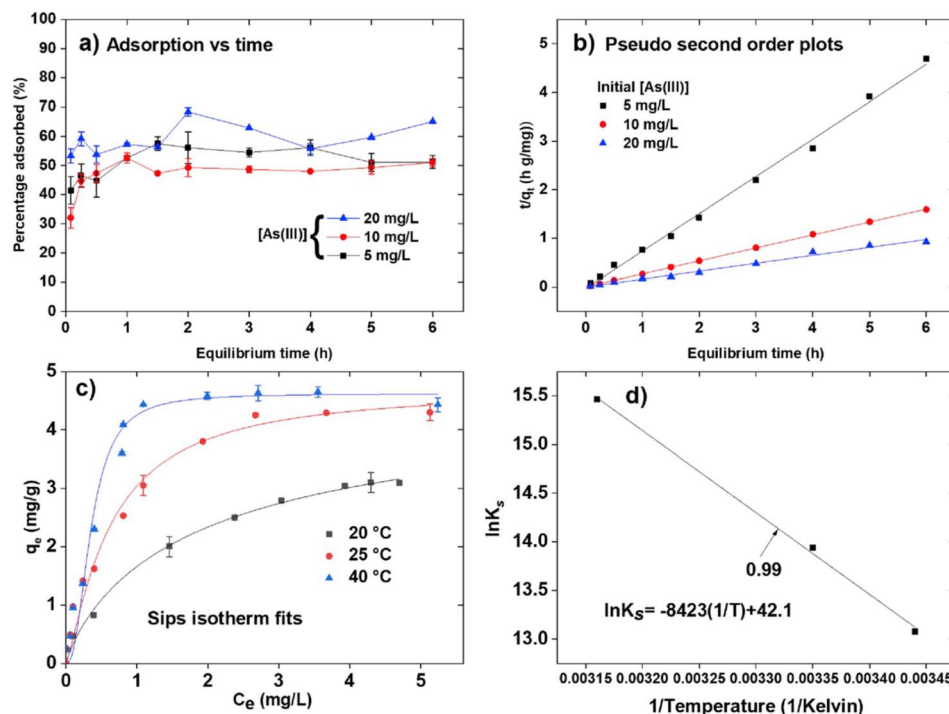


Fig. 7 (a) Adsorption vs. time; (b) pseudo 2nd order model; plots of initial As(III) concentrations of 5, 10, and 20 mg L<sup>-1</sup>; (c) the Sips isotherm fits of As(III) adsorption; and (d) van't Hoff plot of  $\ln K_s$  vs.  $1/T$  for the As(III) adsorption. Reproduced from ref. 95 with permission from Elsevier, copyright 2019.

can interact with the active sites on the adsorbent surface adequately (Table 1).<sup>96</sup>

The humic acid-coated graphene-magnetite nano-composite has shown absorption capacities of 8.67 and 61.73 mg g<sup>-1</sup> for As(III) and As(V) respectively.<sup>97</sup> A novel magnetic composite consisting of Fenton treated pine cone, agricultural waste, and magnetite nanoparticles was prepared and applied to achieve simultaneous arsenite oxidation and adsorptive removal.<sup>98</sup>

Magnetite nanoparticles were synthesized by an eco-friendly green method using onion peel (MNP-OP) and corn silk extract (MNP-CS). Onion peel and corn silk extract are good phenolic compounds to reduce Fe<sup>3+</sup>. The maximal adsorption capacities for MNP-OP and MNP-S were 1.86 mg g<sup>-1</sup> and 2.79 mg g<sup>-1</sup>, respectively.<sup>99</sup> The chitosan/magnetite nanocomposite decreased the amount of As(V) from 0.6 mg L<sup>-1</sup> to less than 0.01 mg L<sup>-1</sup> and could remove As(V) even after several cycle runs effectively.<sup>100</sup> Magnetite-modified water hyacinth biochar has a sorption capacity of 7.4 mg g<sup>-1</sup> for As(V) and the used sorbent could be separated using a suitable magnet.<sup>101</sup> Palm shell waste-based activated carbon (PSAC) magnetized by hydrothermal impregnation of nano-magnetite and then coated by lanthanum effectively removed arsenate with an adsorption capacity of 227.6 mg g<sup>-1</sup>.<sup>102</sup>

**3.2.5 Other magnetite nanocomposites.** Magnetite nanoparticles synthesized using iron ore tailings were used to adsorb arsenate in the presence of Cu<sup>2+</sup>, Zn<sup>2+</sup>, and Mn<sup>2+</sup> at pH = 5.5. It was observed that the adsorption of arsenate was more noticeably affected by the copper, followed by zinc and manganese ions. The maximum amount of adsorbed arsenate was 10.33 mg

g<sup>-1</sup>.<sup>103</sup> Yttrium-doped iron oxide (magnetite and goethite) adsorbed arsenic(III and V) via the linkages of Y-O-As and Fe-O-As. The adsorption capacities are 170.48 mg-As per g and 84.22 mg-As per g for As(V) and As(III) respectively.<sup>104</sup> Boron nitride nanosheets (BNNSs) and Fe<sub>3</sub>O<sub>4</sub>-functionalized BNNS (BNNS-Fe<sub>3</sub>O<sub>4</sub>) nanocomposite were used for the removal of As(V) ions. The highest adsorption capacity (26.31 mg g<sup>-1</sup>) was found for the BNNS-Fe<sub>3</sub>O<sub>4</sub> nanocomposite, whereas the bare BNNS adsorbent had 5.30 mg g<sup>-1</sup> at pH = 2.<sup>105</sup> The fly ash (FA) modified by magnetite (M) showed an adsorption capacity of 19.14 mg g<sup>-1</sup> for As(V). After five consecutive adsorption processes, the adsorption capacity increased to 65.78 mg g<sup>-1</sup> by FAM.<sup>106</sup> Magnetite-rich particles (MEP) were isolated from mill scale (wustite, hematite, magnetite, elemental iron, small amount of oil, and grease) and showed a maximum adsorption quantity of 12.69 mg g<sup>-1</sup> of arsenate on 1 g of MEP.<sup>107</sup>

## 4 Mechanism of arsenic removal by magnetite

The mechanism of arsenic removal by magnetite was explained by many researchers.<sup>108,109</sup> An inner-sphere ligand exchange mechanism is employed to adsorb As(III) and As(V) on magnetite in the form of arsenic oxyanion which exchanges with surface OH or OH<sub>2</sub> groups with Fe<sup>3+</sup> at the iron oxide surface.<sup>110</sup> There are two types of H atoms, *i.e.*, in the inner-sphere complexes and directly attached to the surface which could form the inner-sphere arsenate complexes and FeOH...H hydrogen bond.<sup>111</sup> The absorbed As(V) anions are generally coordinated to two

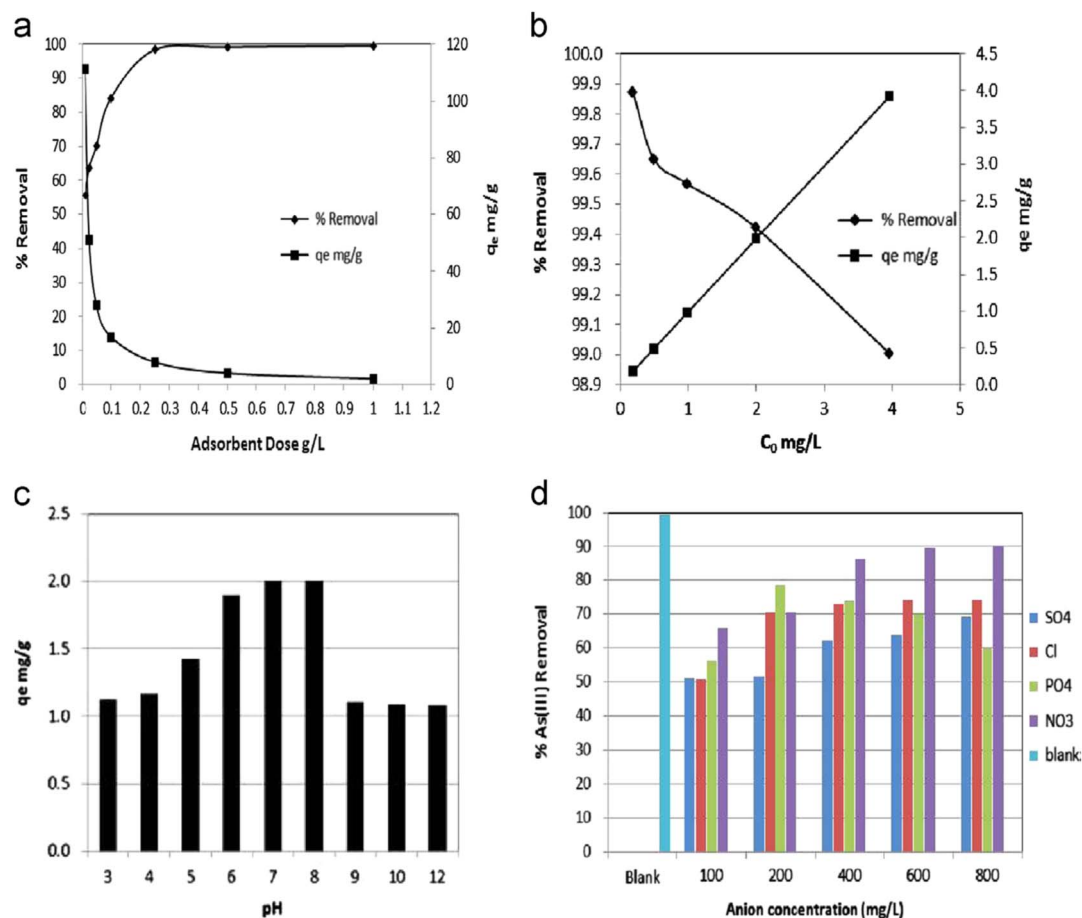


Fig. 8 (a) Effect of adsorbent dose, (b) effect of initial As(III) concentration on As(III) adsorption, (c) effect of pH, and (d) effect of interfering anions on As(III) adsorption, using MION-tea. Reproduced from ref. 96 with permission from Elsevier, copyright 2014.

adjacent  $\text{Fe}^{3+}$  cations on the magnetite surface and form a surface complex known as a bidentate binuclear-bridging complex [Fig. 9(a)]. However, iron oxide adsorbs As(III) *via* both bidentate binuclear-bridging complexes and monodentate complexes. In the monodentate complex, a single oxygen atom from the As(III) oxyanion is coordinated to  $\text{Fe}^{3+}$  cations on the magnetite surface [Fig. 9(b)]. The main bonding mechanism of As(III) could include either a monodentate bond or the formation of an outer-sphere complex. In the outer sphere complex, the ligand is bound to the surface OH or  $\text{OH}_2$ , possibly by a hydrogen bond [Fig. 9(c)].<sup>92</sup>

## 5 Future outlook and challenges

Clean water is an essential requirement of all living beings. There is an urgent need of the hour to find economically feasible, recyclable, and eco-friendly adsorbents for water treatment. Arsenic is the most hazardous contaminant in water. Iron-based nanomaterials could be the future of water purification due to their low cost and convenient technologies. This review reveals the importance of magnetite nanomaterials and their composites to treat water efficiently by removing arsenic impurities from the contaminated water. These materials are

ideal due to their high surface-to-volume ratio, control of morphology, easy magnetic separation, reusability, and high efficiency. Magnetite nanomaterials could separate out the contaminated ions or particles *via* magnetic separation methods which can reduce the cost as compared to traditional methods such as centrifugation, filtration, sedimentation, *etc.*

Adsorption is considered the most effective method to remove arsenic contamination. Practically, there could be a challenge with agglomeration in magnetite nanomaterials due to their high magnetization. However, these challenges could be tackled by using suitable composites of these materials. There should be a focus on research to find the toxicity and likely health effects. These materials should be studied properly for any hazards to the health and environment. Future research should be based on removing arsenic as well as other toxic impurities from wastewater. It should be kept in mind that these removal techniques keep good and essential minerals in the water intact.

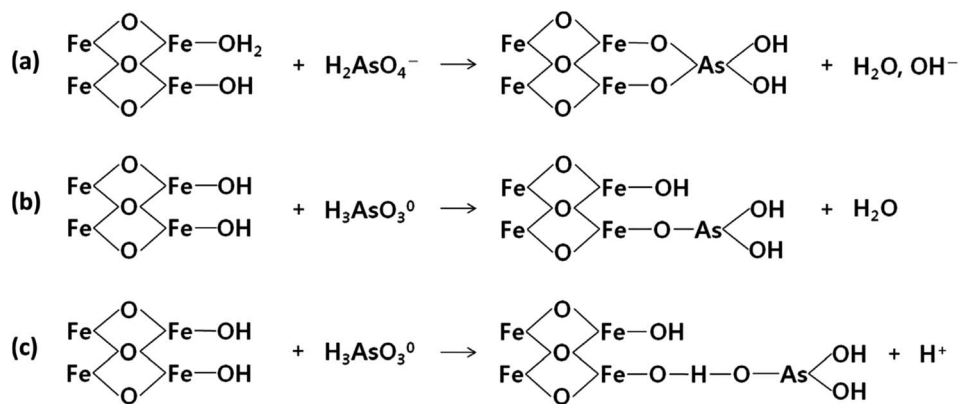
Magnetite and its nanocomposites should be explored for removing different heavy metals such as Hg, Cd, Cr, Pb, *etc.*, and other pollutants from wastewater. These water cleaning techniques should be commercialized in near future. It could be done as a multidisciplinary study for chemists, engineers,





**Table 1** Arsenic adsorption behavior of magnetite nanomaterials and their composites

| Adsorbent                                                                                   | Adsorption capacity ( $Q_{\max}$ in $\text{mg g}^{-1}$ )                              | Ref. |
|---------------------------------------------------------------------------------------------|---------------------------------------------------------------------------------------|------|
| Magnetite/non-oxidative graphene (M-nOG) composites                                         | 32.7 $\text{mg g}^{-1}$ for As(III)<br>13.1 $\text{mg g}^{-1}$ for As(V)              | 16   |
| Magnetite-silica                                                                            | 170 $\mu\text{mol g}^{-1}$                                                            | 46   |
| Magnetite coated sand                                                                       | 6695 $\mu\text{g L}^{-1}$                                                             | 87   |
| Magnetite-graphene oxide composites (M-GO)                                                  | 85 $\text{mg g}^{-1}$ for As(III)<br>38 $\text{mg g}^{-1}$ for As(V)                  | 92   |
| Magnetite-reduced graphene oxide composite (M-rGO)                                          | 57 $\text{mg g}^{-1}$ for As(III)<br>12 $\text{mg g}^{-1}$ for As(V)                  |      |
| MION-tea                                                                                    | 188.69 $\text{mg g}^{-1}$ for arsenic(III)<br>153.8 $\text{mg g}^{-1}$ for arsenic(V) | 96   |
| Humic acid coated graphene- $\text{Fe}_3\text{O}_4$ nanocomposites                          | 8.67 $\text{mg g}^{-1}$ for As(III)<br>61.73 $\text{mg g}^{-1}$ for As(V)             | 97   |
| Pine cone magnetite nanoparticles composite                                                 | 17 $\text{mg g}^{-1}$ for arsenic(V)                                                  | 98   |
| Chitosan-coated magnetite nanoparticle                                                      | 10.81 $\text{mg g}^{-1}$ for As(V)                                                    | 100  |
| Magnetite-modified water hyacinth biochar                                                   | 7.4 $\text{mg g}^{-1}$ for As(V)                                                      | 101  |
| Magnetized PSAC                                                                             | 227.6 $\text{mg g}^{-1}$ for arsenate                                                 | 102  |
| Magnetite/ $\text{Cu}^{2+}$                                                                 | 10.33 $\text{mg g}^{-1}$                                                              | 103  |
| Yttrium-doped magnetite and goethite                                                        | 170.48 $\text{mg-As per g}$ for As(V)<br>84.22 $\text{mg-As per g}$ for As(III)       | 104  |
| $\text{Fe}_3\text{O}_4$ -functionalized BNNS (BNNS- $\text{Fe}_3\text{O}_4$ ) nanocomposite | 26.31 $\text{mg g}^{-1}$ for As(V)                                                    | 105  |
| Boron nitride nanosheets (BNNSs)                                                            | 5.30 $\text{mg g}^{-1}$                                                               |      |
| Fly ash by magnetite                                                                        | 65.78 $\text{mg g}^{-1}$                                                              | 106  |
| MNP-OP                                                                                      | 1.86 $\text{mg g}^{-1}$ for As(III)                                                   | 107  |
| MNP-CS                                                                                      | 2.79 $\text{mg g}^{-1}$ for As(III)                                                   |      |

**Fig. 9** The mechanisms of arsenic adsorption (a) As(V) and (b), (c) As(III) by magnetite nanocomposites. Reproduced from ref. 92 with permission from Elsevier, copyright 2016.

material scientists, and biologists worldwide. These materials have shown reusability which could be cost-effective as well. It is our duty to save clean water for our future generations.

## 6 Conclusion

Arsenic is a highly toxic metal ranking one in toxicity. Efforts have been made to remove this harmful metal from water but could not be successful due to various pros and cons. Researchers have been exploring new techniques and methods to purify water. Magnetite nanomaterials and their composites are considered excellent materials to purify water because of their high magnetization, adsorption behaviour, and

biodegradability. These nanomaterials and their composites are cost-effective as well as they can be easily separated, regenerated, and reused. This review gives an overview of the potential of magnetite nanoparticles and their composites to treat contaminated water and remove unwanted arsenic impurities. These materials could be explored to clean water from harmful contamination.

## Conflicts of interest

The authors declared that they have no conflicts of interest related to this work. I declare that I do not have any commercial or associative interest that represents a conflict.



## Acknowledgements

The author declares that no funds, grants, or other support were received during the preparation of this manuscript.

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