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New Generation Nanoadsorbents and Conventional Techniques for Arsenic Removal from Waters

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Abstract: Nowadays, with excessive use due to rapid population growth, growing industry, and technological developments, environmental pollution is also increasing and is reaching a point where it threatens the health of humans. The alarming increase in environmental pollution is mostly seen in the form of water pollution. Water pollution has reached levels that threaten human health. There are difficulties in accessing clean water in many parts of the world as a result of restricting the use of natural water resources polluted by both human activities and natural causes. Therefore, intense efforts are made to remove especially heavy metals and other harmful substances that pollute water. Among these toxic heavy metals threatening the health of humans, arsenic is at the top of the list as the most dangerous one. In recent years, many methods and techniques have been developed in addition to classical methods for removing pollutants from water. In this study, conventional methods used in the treatment of arsenic-contaminated waters, the difficulties encountered in the removal process, and the advantages and disadvantages of the methods were critically reviewed in the light of current and past information. In addition, detailed comparative information is given about nano-sized adsorbents, which is an innovative approach used in the adsorption method, one of the arsenic removal methods.

Keywords: Arsenic, arsenic removal, removal methods, nanoadsorbents, adsorption

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1. INTRODUCTION

The presence of arsenic in water sources is a common problem in the world. Arsenic is one of the 20 most abundant natural elements in the earth's crust. Arsenic is an odorless and tasteless semi-metal with atomic number 33 and atomic weight 74.91. Arsenic is found as a basic component in more than 200 minerals. Arsenic is mostly found in sulfur and oxides of different minerals. Arsenic is found in sulfur minerals such as arsenic sulfide or orpiment (As_2S_3), realgar (AsS), arsenopyrite (FeAsS) (1-3).

Arsenic level in water is increasing due to natural and anthropogenic reasons. Arsenic pollutes water through the erosion and dissolution of rocks, minerals and ores in the soil or through natural events such as geothermal and volcanic activities. In addition, arsenic and its compounds are used in various industrial activities such as production of medicines, agricultural chemicals, colorants and dyes, soaps, ceramic, glass, timber, wood, animal skins, cellulose and paper, battery plates, semiconductor production and petroleum refining and electroplating processes. Even natural events are the most important cause of arsenic pollution in water, the discharge of wastewater from various industrial enterprises, agricultural practices and mining activities into the environment without being subjected to adequate treatment processes is also a very important factor (3).

Arsenic exists in nature as both organic and inorganic compounds. Inorganic arsenic compounds are the most common. Arsenic is commonly seen in water in two oxidation states: arsenite (As^{3+}) and arsenate (As^{5+}). In natural waters, under different redox conditions, arsenic exists in (3-), (0), (3+) and (5+) oxidation stages (1).

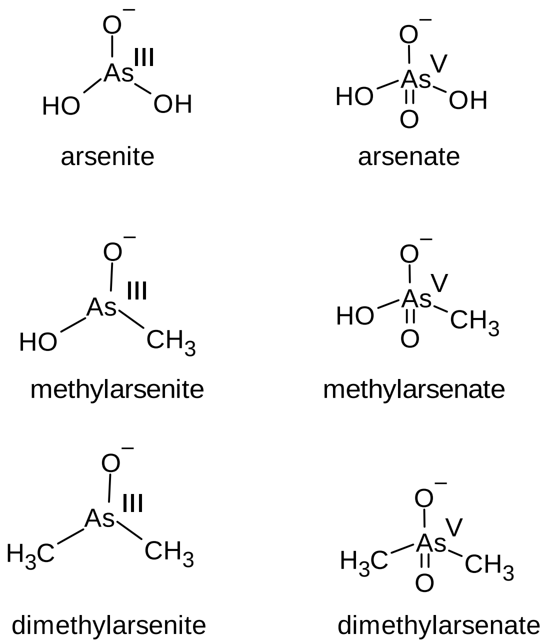

Figure 1: Arsenic species commonly found in water. Figure republished with permission from Ref. (9).

Depending on the pH of the medium, while in oxidizing conditions arsenic ions are found in waters as arsenate [As(V)] species H_3AsO_4, $H_2AsO_4^-$, $HAsO_4^{2}$, and in reducing conditions it is found as arsenite [As(III)] species H_3AsO_3, $H_2AsO_3^-$, $HAsO_3^{2-}$ (1).

Which species of arsenic will be dominant in the aquatic medium depends on the pH value and redox potential (Eh) of the water. Generally, arsenic is present in surface waters in the form of As(V), and As(III) is present in groundwater in anaerobic conditions with low oxygen content (2). In choosing the arsenic removal method, it is very important which species of arsenic is in the medium.

Table 1: Different species of Arsenic found in aqueous media depending on the pH of the medium. Figure reproduced with permission from Ref. (4).

Reaction	**pKa**
As (V)	
$H_2AsO_4^- + H^+ \rightarrow H_3AsO_4$	2.24
$H_2AsO_4^{2-} + H^+ \rightarrow H_2AsO_4^-$	6.96
$H_2AsO_4^{3-} + H^+ \rightarrow H_2AsO_4^{2-}$	11.50
As (III)	
$H_2AsO_3^- + H^+ \rightarrow H_3AsO_3$	9.22
$H_2AsO_3^{2-} + H^+ \rightarrow H_2AsO_3^-$	12.11
$AsO_3^{3-} + H^+ \rightarrow HAsO_3^{2-}$	13.41

In this graph, also known as the "Pourbaix diagram" in Figure 3, the pH value of the solution is given on the horizontal axis, and the redox potential (Eh) is given in volts on the vertical axis. According to the diagram, arsenite is mostly found in groundwater and arsenate is found in surface waters (1, 3).

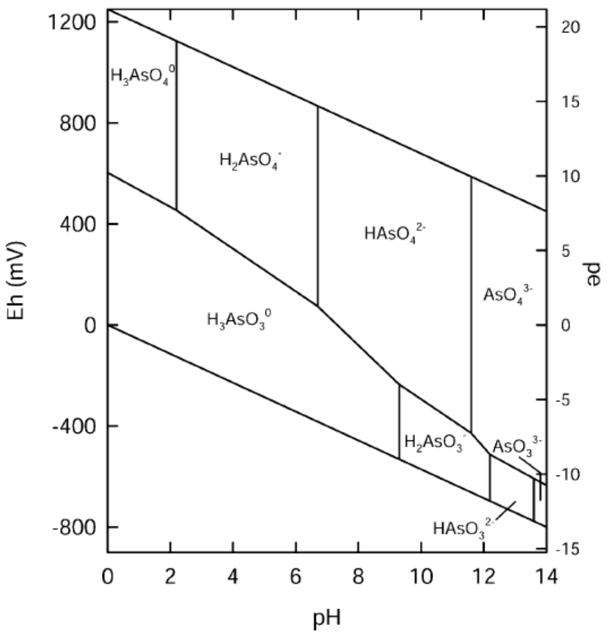

Figure 2: Eh-pH diagram of arsenic species in water in the As-O_2 - H_2O system (25 °C temperature and 1 bar total pressure). Figure republished with permission from Ref. (1).

It is very difficult to remove uncharged arsenite ions at the pH levels of drinking water. Arsenate is present in water as oxyanions. These oxyanions can be easily removed from solution by precipitation, adsorption, ion exchange and some other methods. Therefore, in order to remove arsenite, it must first be oxidized to arsenate. In other words, uncharged arsenite must be made charged. Removal of arsenic species from solution does not depend only on the oxidation stage of arsenic. In addition, it also depends on other factors such as the presence of other ions in the solution (2, 3).

1.1. Arsenic Pollution and Its Effects on Health

Arsenic pollution is a major problem in natural water resources around the world. High levels of arsenic contamination in underground and surface waters have been reported in many countries such as the United States, Argentina, Bangladesh, China, India, Japan, Cambodia, Canada, Mexico, Mongolia, Nepal, Pakistan, Chile, Thailand, Taiwan, Turkey, Vietnam and New Zealand. Bangladesh and the West Bengal region of India are the most populated regions exposed to arsenic from groundwater (2).

Although it was used in the past to treat diseases such as syphilis and amoebic dysentery, arsenic is now listed among the first group of carcinogenic compounds by the World Health Organization (WHO) and the International Agency for Research on Cancer (IARC). Based on research, the World Health Organization determined the maximum amount of arsenic in drinking water as 10 μg/L in 1993 and declared that water containing arsenic above this value is toxic (3,4). As(III), one of the most common inorganic arsenic species found in water, is the most toxic form of arsenic. Arsenite is 60 times more toxic than arsenate, and inorganic arsenic is 100 times more toxic than organic arsenic. The toxicity level of arsenic is listed as "Arsine > arsenite As(III)>

Organic As(III)> arsenate As(V)> organic As (V)> arsonium" (3).

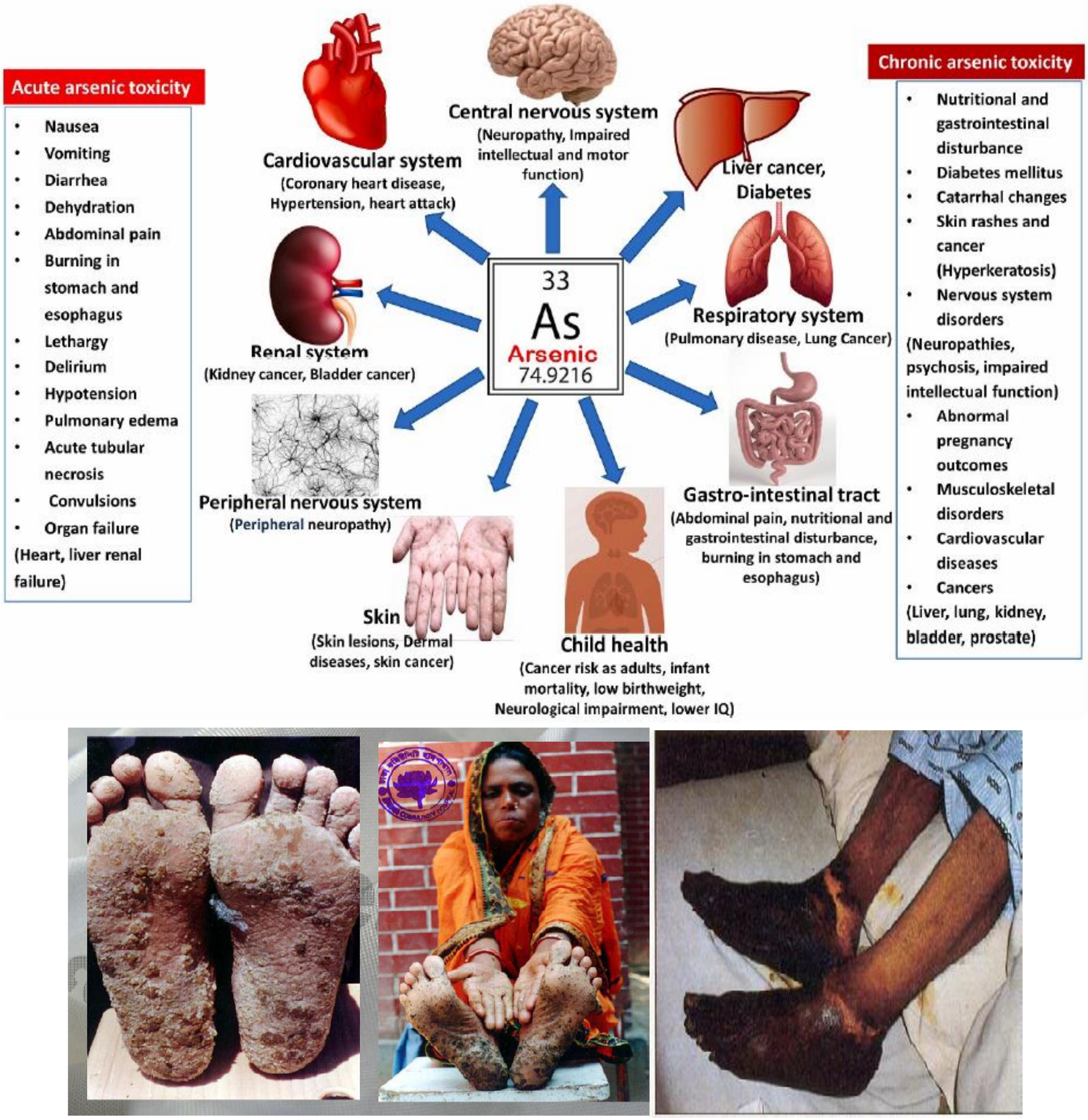

Figure 3: Human health effects of exposure to arsenic. Figure republished with permission from Ref. (12).

Arsenic is generally taken into the human body through drinking water and accumulates in tissues over time. Arsenic disrupts the structure of enzymes and proteins in the body, renders them dysfunctional, and even causes damage to molecules such as DNA and RNA in long-term high intakes. The disease symptoms that occur when water contaminated with arsenic is drunk for several years are called arsenicosis. The effects of exposure to arsenic through drinking water include various skin lesions, neurological effects, hypertension, cardiovascular diseases, respiratory disorders, diabetes, edema, gangrene, ulcers, skin and other types of cancer, miscarriage, stillbirth, premature births, weakness, weight loss, lethargy, anemia, and damage to the immune system (3-6).

Arsenic combines with some enzymes in the body and disrupts cellular metabolism. The fact that arsenic has a special affinity for sulfur is the main reason why it is toxic to the body. Arsenic, by binding to the free thiol groups in the protein part of some enzymes, inhibits the enzymes and so renders them inoperable (3, 7, 8).

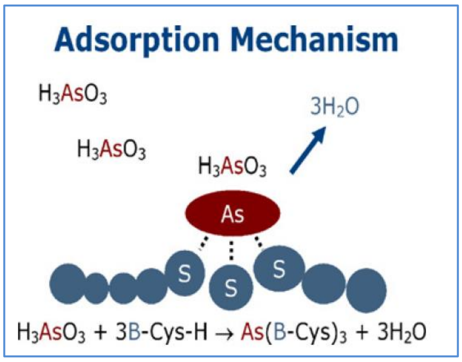

Figure 4: Schematic representation of the complex formed by an arsenic atom with 3 -SH thiol molecules. Figure republished with permission from Ref. (6).

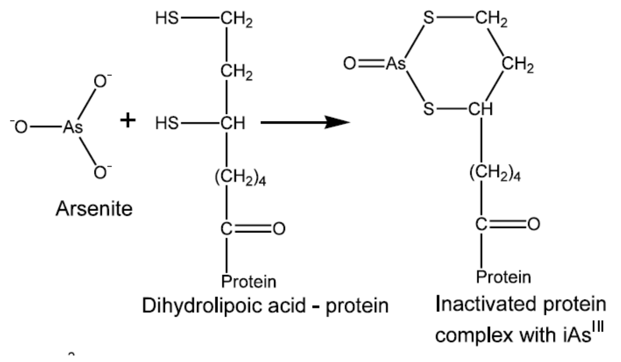

Figure 5: Arsenic blocks the enzyme system. Figure republished with permission from Ref. (3).

Arsenic shows its effects by causing the cells' mitochondrial enzymes to lose their activity. As(III) compounds have a high affinity for sulfhydryl groups found in proteins and form chelation with these groups. As(V) competes with phosphate in cell reactions and prevents ATP formation by separating oxidative phosphorylation (8-10).

2. ARSENIC REMOVAL METHODS FROM WATERS

Drinking water is often treated to remove turbidity and kill microorganisms. There are many technologies developed for the removal of arsenic from drinking and groundwater. These technologies are used effectively today, with arsenic removal of up to 95% in various sizes, from household to classical treatment plant scale. The chemical properties and composition of arsenic-contaminated water and the intended use of the treated water are among the factors that determine which technologies should be used in purification. Especially when arsenic removal is aimed, different processes are applied depending on the flow rate and application location. When choosing an effective arsenic removal process, pH should be taken into account depending on the species of arsenic. If As(III) is present in the medium, the uncharged As(III) must be oxidized with oxidizers such as Cl_2, NaOCl, $KMnO_4$, O_3 etc. to As(V) through a pre-treatment process. Since groundwater is generally anaerobic, all arsenic compounds are generally found in the As(III) form, depending on the conditions of the medium. Since As(III) is uncharged at the natural pH level and As(V) is negative at the natural pH level, removal of As(V) is easier (4-6, 9).

Technologies traditionally applied to remove arsenic species from water are oxidation, coagulation-flocculation, adsorption, ion exchange and membrane techniques.

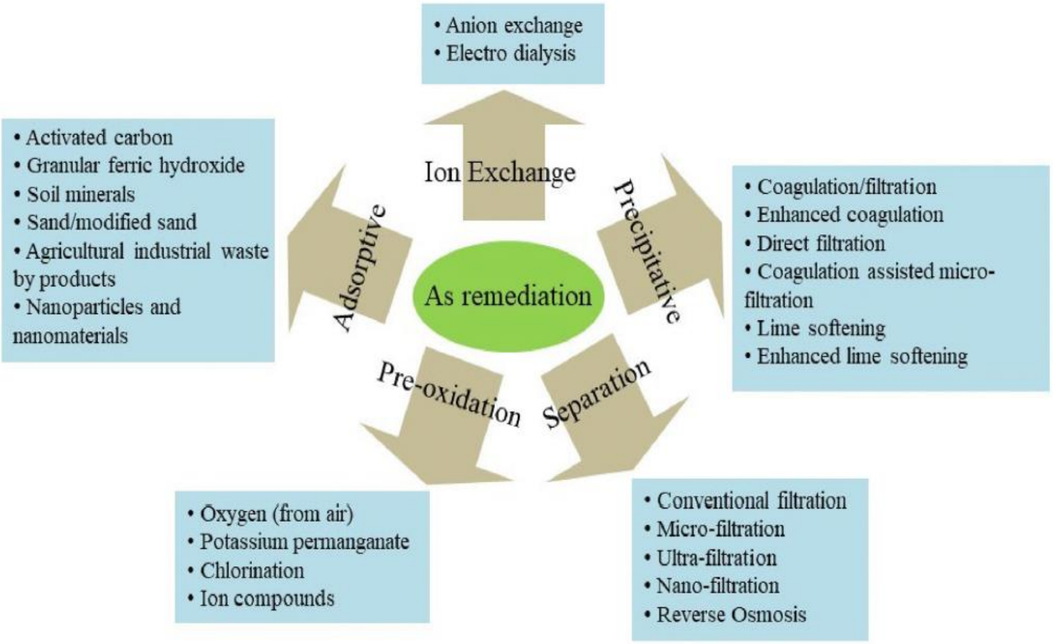

Figure 6: Conventional arsenic removal methods from water. Figure republished with permission from Ref. (5).

Coagulation-sedimentation and filtration processes are also used for the purpose of remove arsenic at the source in high-flow drinking water treatment. For small flow rates and points of use, membrane purification processes such as adsorption, ion exchange, reverse osmosis and nanofiltration can be applied. Below, all arsenic removal processes are discussed with their positive and negative aspects (2, 5, 11).

Considering the disadvantages of the processes used in arsenic removal, it could be said that an alternative arsenic treatment process which has some important properties should be developed. The followings could be given as an example to these properties; 1) it should has high arsenic removal efficiency and high effectiveness in removing both species of arsenic, 2) it should not require pre-oxidation process and additional chemicals, 3) it should not create secondary pollutants in the treated water, 4) it should creates less treatment sludge and waste, 5) it should has low operation and maintenance-repair costs (12, 13).

2.1. Overview of Common Arsenic Removal Methods as Removal Technologies

2.1.1. Arsenic removal by coagulation

The most commonly used methods for removing arsenic from drinking water are coagulation-precipitation and filtration methods. Chemical precipitation is the most used method on industrial scale because it is highly effective, relatively easy to apply and low cost. Arsenic removal by chemical precipitation method is based on the principle of formation of a poorly soluble common salt. Arsenic becomes dissolved in the medium and precipitates by adsorption on the surface of metal hydroxides or by mixing with the structure during floc formation (14). With this type of purification method, in addition to arsenate, many solid substances such as turbidity, iron, manganese, phosphate and fluoride are also removed. The most commonly used coagulants in this method include Fe^{3+} and aluminum salts. Additionally, this technique is used in large-scale treatment processes such as urban treatment plants by adding lime softener (10, 15). The most commonly used chemicals are lime ($Ca(OH)_2$), ferric chloride ($FeCl_3.nH_2O$) and aluminum sulfate ($Al_2(SO_4)_3.nH_2O$). It is possible to remove arsenic at a rate of 90% with lime, 90% with aluminum sulfate and 95% with iron compound (16).

In the chemical precipitation process, heavy metal ions are precipitated by converting them into insoluble salts with a chemical agent added to the medium. By adding coagulant to water, the ability of colloidal particles to come together in water is increased. With the added coagulants, aluminum or iron hydroxide microflocs are rapidly formed. The flocs grow until they reach sufficient weight and then precipitate. Thus, it is purified from the water medium. Gravitational force and friction force are effective on the precipitated particles (16, 17).

Studies have been conducted investigating the pH effectiveness of different coagulants in arsenic removal. However $Al_2(SO_4)_3$ and $FeCl_3$ exhibited equal performance in arsenic removal in waters with pH below 7.3, it was observed that $FeCl_3$ was a more effective coagulant in waters with pH greater than 7.3. While aluminum hydroxide is stable in the neutral pH range, iron hydroxide is stable in a wider pH range. Additionally, since iron hydroxides have a high affinity for arsenic, co-precipitation of arsenic with iron hydroxide occurs. If As(III) is present in the water, first As(III) is converted to As(V) by oxidation and pH adjustment, and then As(V) is removed by the coagulation-filtration process (16-18).

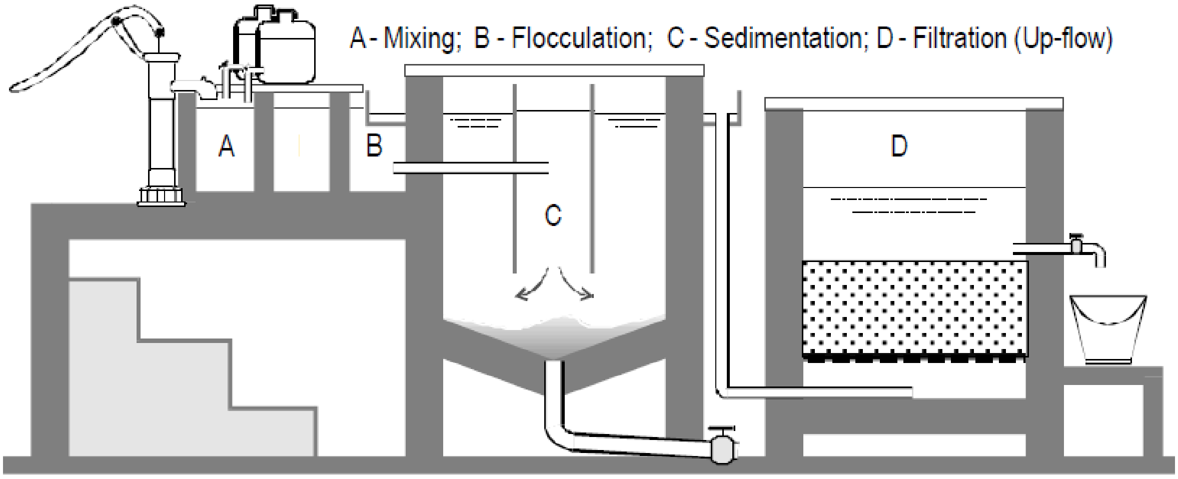

Figure 7: A facility where coagulation-sedimentation and filtration processes can be carried out simultaneously. Figure republished with permission from Ref. (19).

Coagulation- Filtration process produces sludge (if a sedimentation tank is used) and backwash water (if a filter is used) as waste. The water content of the sludge coming from the sedimentation ponds is quite high, so the solids content is quite low (SM < 1%). For this reason, it is recommended to increase the solids content with sludge thickeners before dewatering. The solids content can be increased to 35-50% with a filter press and 15-30% with a centrifuge. Depending on the arsenic content, the resulting sludge can be disposed of by dumping it on land or by burying it in regular storage facilities. Lime-Soda method is a chemical treatment process in which coagulation, flocculation and precipitation processes are applied. Lime softening is another economical, conventional treatment process that is effective for arsenic removal. In the lime soda softening method, the optimum pH for As(V) and As(III) purification is expressed as approximately 10.5 and 11, respectively. Arsenic a result of the lime-soda process, sludge emerges as waste and pH adjustment is needed again. Typical sludge concentration contains 1-4% arsenic waste (10, 18, 19).

2.1.2. Oxidation

The chemical form of arsenic is important in its purification. Since arsenic in groundwater is generally found in the uncharged As(III) form, it must first be converted to As(V) form in order to be effectively removed from the water. Arsenic in water is not removed by oxidation, but arsenite is oxidized to arsenate and removed in subsequent processes (chemical precipitation, filtration, membrane processes, etc.). Adding oxidants such as chlorine, permanganate, ozone, chlorine dioxide and hydrogen peroxide helps to increase the oxidation rate of arsenic. Among these, chlorine is a fast and effective oxidant for arsenic due to its easy accessibility. However, it is known that chlorine may create some toxic by-products (trihalides) as a result of its reaction with organic substances (18, 19).

When native iron is present in groundwater, oxidation and coprecipitation are followed by cost-effective filtration that removes waste. In oxidation by co-precipitation, iron is oxidized from Fe^{2+} to Fe^{3+} and arsenic is oxidized from As(III) to As(V) and they are filtered from water. Iron and arsenic As(III) are oxidized, then arsenic As(V) is adsorbed to iron hydroxide compounds and retained in the filters. The ratio between iron and arsenic should be 20:1 (10, 12). The appropriate pH range for the retention of arsenic compounds with iron is stated as 5.5 – 8.5. While oxygen is only sufficient for iron, it cannot oxidize arsenic. Ozone (O_3) is used for disinfection, oxidation, odor and taste removal (10).

2.1.3. Arsenic removal with membrane processes

Another effective treatment technology used in removing arsenic from water is membrane technologies. Membrane processes are generally used to purify groundwater and drinking water where clogging is not observed due to sediment formation. In these processes, separation is carried out according to the molecular size, shape or charge of the substance. For example, if the important criterion is the molecule size, while water and other small molecules can pass through the membrane, molecules and particles larger than water cannot pass (10, 17). In porous membranes, the separation process is achieved by passing mixture which has more than one component through the membrane. Membranes are an effective method for arsenic treatment. What is expected from the membrane process is that even low amounts of arsenic species in the water can be eliminated from the water with high efficiency.

Such techniques have advantages such as high removal efficiency, easy operation, and minimal toxic sludge generated during the process. However, the initial investment and operating costs are relatively high, and high pressure is usually needed to pass contaminated water through the membranes. In addition, in the membrane process, discharge of concentrate, membrane clogging and flux reduction are generally inevitable (20-23).

Generally, four different membrane processes are applied in water treatment. These are microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO). These processes differ from each other due to the difference in pore size. As the selectivity of the membrane increases, the pressure used in the process also increases. While separation is achieved through mechanical sieving at low pressure for MF and UF membranes, separation occurs by capillary flow or solution diffusion at high pressure for NF and RO membranes. UF and MF membranes are generally used for particle and removal of pathogens. UF membranes can remove disinfection by-products to a large extent. MF membranes have on average ten times larger pores than UF membranes. MF membranes are designed to remove micrometer-level contaminants. It has a pore structure between 0.05 and 5 micrometers. While UF membranes can purify viruses, viruses can pass through the pores of MF membranes (22).

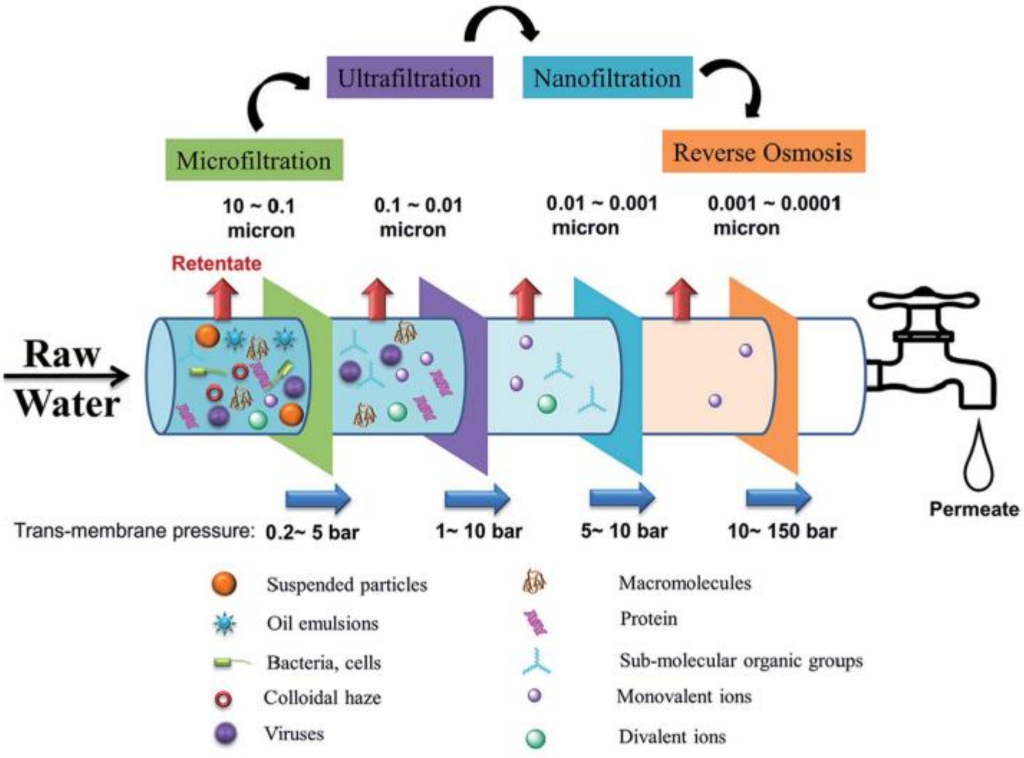

Figure 8: Membrane technologies. Figure republished with permission from Ref. (20)

Nanofiltration is also a very effective method in arsenic purification. However, investment and operating costs are high and it generates wastewater. Since it can remove all pollutants from water at a high rate, it provides quality drinking water production. Cellulose (cellulose acetate (CA) or cellulose triacetate CTA) membranes are generally used in nanofiltration. The largest advantage of these membranes is that they are resistant to chlorinated water. Despite this, they are adversely affected by alcoholic liquids and some bacteria. Membrane performance can be increased by appropriate pre-treatment of raw water with coagulation chemicals, pre-filtration and hardness removal methods (19, 24).

Osmosis; in nature, it occurs by the transfer of water from one to the other between two liquids of different concentrations, between which there is a semi-permeable membrane that allows only water to pass through and impermeable to other substances, and this process continues until balance is achieved on both sides. Osmotic pressure occurs with the static height difference caused by the volume change in the liquids on both sides of the membrane. Reverse osmosis, on the other hand, is a membrane technology and is the process of passing mineral-rich water with reduced minerals to the other side of a semi-permeable membrane by using osmotic pressure. Many minerals, bacteria and viruses in water can be removed with this method up to 99% purity. Reverse osmosis is relatively simple compared to similar technologies (23, 24).

Factors affecting the performance of the membrane process are suspended solids, high molecular weight dissolved solids, organic compounds and colloids, oxidation species of arsenic and temperature. High molecular weight particles in the membrane feed water can cause clogging of the membrane. Before the membrane process, pre-oxidation of arsenic species in the water to be treated will increase the treatment efficiency. As(III) compounds are smaller than As(V) compounds and pass through the membrane more easily than arsenate. Membrane technology can also be used as a polishing step after other treatment technologies in cases where solids are removed from the precipitation process and lower arsenic concentrations are required (19, 24).

2.1.4. Arsenic removal by ion exchange

Ion exchange technology is a physical and chemical process in which ions held by electrostatic forces on the surface of the resin are replaced by ions with similar charge values in the water. It is a method based on the principle of keeping the anions and cations desired to be purified from wastewater in a column filled with a suitable anion and/or cation exchanger (19). In ion exchange, arsenic is purified by exchanging the ions dissolved in water with an ion in the ion exchanger. Ions with a strong bond structure are replaced by ions with a weak bond structure in the water medium. Resins used in ion exchange are resins made from synthetic organic, inorganic or natural polymeric materials. There are two types of resins: anion and cation resins. Anion resins are generally used for chlorine and anionic pollutants, while cation resins are used for sodium, potassium and cationic pollutants. Mixed resins are used in cases where both types of pollutants are present. The resin is generally placed in the column, and as the arsenic water passes through the column, the arsenic ions are replaced by ions such as chloride or hydroxide on the resin surface, depending on the type of resin used. Anion exchange resins used in the removal of arsenic from water are resin systems in which As(V) ions are removed by effectively replacing the $H_2AsO_4^-$, $HAsO_4^{2-}$ and AsO_4^{3-} oxy-anionic species of arsenate with the anionic charged functional group of the resin. Since arsenite is generally found as a neutral molecule, an oxidation step is applied as a pre-treatment for using the ion exchange method. Common competitive anions such as sulfate, phosphate and nitrate are important in the removal of Arsenic by ion exchange. Ion exchange resin must be regenerated periodically (19, 25).

Various strong base-based ion exchange resins are easily available in the market and are used effectively to remove arsenate from water. As a result of removal, arsenic concentration can be reduced below 1 μg/L. Although nitrate-selective resins also remove arsenic, classical sulfate-selective resins are particularly suitable for arsenate removal (25). Generally, resins are pretreated with HCl acid to generate chloride ions on the surface. These resins can also be made ready for use with other anions such as bromide or acetate. Chloride is easily replaced by As(V). After arsenite is converted to As(V), it is eliminated very efficiently with anion exchange resins. As the pH of the water medium increases from pH 6.5 to pH 8.5, the adsorption capacity of the ion exchanger decreases. As(V) removal is relatively independent of pH and inlet water concentration. On the other hand, among anions, especially sulfate has a strong effect. Because the ion exchange resin prefers to retain sulfate before arsenate. Therefore, it is preferred to have low sulfate concentration in raw water (2, 19).

2.1.5. Adsorption

Adsorption is the process of adhesion of ions, atoms or molecules to the surface of a solid material. Adsorption processes are one of the most useful methods preferred in purification. This method is based on the principle of removing ions from the water medium by adhering to a solid adsorbent surface in water purification processes. In this method, the interaction between the adsorbent substance and analyte ions is generally reversible (2, 4, 19).

In adsorption purification technology, adsorbent is placed in the column. While water containing arsenic passes through the column, the pollutant adsorbed to the adsorbent surface with the help of physical and chemical forces, thus removing arsenic from the water. Arsenic adsorption largely depends on the concentration of the system, its pH, and the type of absorbent used (12, 19). Many materials are used as adsorbents. Many organic or inorganic substances can be given as examples of these adsorbents such as activated alumina, activated carbon, granular ferric hydroxide, pulp coated with ferric hydroxide, sand coated with iron oxide, sand mixed with iron fillings, green sand filtration (potassium permanganate coated gluconite), copper-zinc granules, zeolite modified with surfactant, dried hyacinth root, jute, red ash, fly ash, sawdust, and newspaper pulp. Adsorbents used in the adsorption process must be stable, economical, regenerable and reusable. The surface area of the adsorbent used in adsorption, the volume and size distribution of the pores are important because they affect the adsorption capacity and duration. In addition, the surface properties of the adsorbent determine the selectivity of adsorption (19, 26, 27).

Adsorption processes are operations with high efficiency, low cost, ease of use and simple operation. There is no need to add additional reagents to the medium. They do not create by-products and hazardous waste sludge. One of the important advantages of the adsorption method is that the working conditions are flexible and can be adjusted according to need. The regeneration process of the adsorbent is carried out by using appropriate desorption agents, thus it is allowed to reuse of the adsorbent. The reusability of the adsorbent provides a significant economic advantage. Due to all these advantages, adsorption is considered the best available technology (BAT) by EPA (19, 27, 28).

While technologies of adsorption are less used in large-scale classical treatment plants, they are frequently used in treatment technologies used especially for domestic and smaller population settlements. The adsorption method is also applied as a final polishing step in classical treatment systems (12, 19).

3. NANOADSORBENTS FOR ARSENIC REMOVAL FROM WATERS

Advances in nanoscience and nanotechnology have enabled the development of various nanomaterials for environmental applications and the remediation of arsenic-contaminated water. Nanoparticles are atomic clusters smaller than 100 nm (29). Nanoadsorbents are materials that are used in the widely preferred adsorption method in arsenic treatment and are promising for future studies with their unique physical and chemical properties. Properties such as large surface area, high specificity, high reactivity and catalytic potential make nanoparticles excellent candidates for water purification applications (29, 30). The low surface area and slow adsorption speed of conventional adsorbents limit their application. Due to their high surface area, nanoadsorbents allow reaching high adsorption capacities in a much shorter time than micron-scale adsorbents. Among the nanoadsorbents, especially polymeric adsorbents, can be used again and again because they enable surface modification and can be regenerated. Nanoadsorbents have been the most used and researched adsorbents in the treatment of arsenic-contaminated water in recent years (12, 15, 16, 29, 31).

There are different methods in the literature for water treatment applications of nanoadsorbents. Adsorption processes with nanoparticles have generally been applied in the batch method instead of fixed bed column due to the very small size of nanoparticles. There are experiments in which the column inlets and outlets were closed with glass wool to prevent the escape of nanoparticles into the purified water, but no effective results were obtained (27, 32).

Another approach to the applicability of nanoadsorbents in the removal of arsenic from water is the immobilization of nanoadsorbents on appropriate supports. This method, which does not require an additional separation step, causes a decrease in the adsorption ability of the nanoadsorbent. Studies on different solid porous materials such as silica, carbons, polymers, exchange resins, bentonite, kaolinite, zeolites or chitosan beads have been reported (33-37).

From studies related to this approach, Savina et al. produced polymeric composite materials in which iron nanoparticles were embedded in the walls of a macroporous polymer. and the study examining their efficiency in removing As(III) from aqueous media is a good example (38).

Similar to this approach, the study conducted by Önnby et al. is a study on arsenic removal from water with cryogel columns. In the study where cryogels with 3 different properties were synthesized, in the first of the prepared cryogel columns, the surface of the column was prepared by embedding aluminum nanoparticles, the second column was prepared by embedding molecularly imprinted polymers, and the last column was prepared by functionalizing the surface of the cryogel with thiol. The stability of the nanoparticles was ensured by embedment into the polymeric column, and it was reported that maximum adsorption capacities were reached in the pH range of 2-8 in the adsorption carried out in both composite columns (39, 40).

In another study conducted by Gurbuz et al. on arsenic removal with cryogels, they succeeded in removing up to 95.4% of arsenic from groundwater with the cryogel column they prepared. They reported that the poly (HEMA-co-GMA) cryogel hybrid column they synthesized adsorbed As(III) 11.44 and As(V) 5.79 mg/g at pH: 7, respectively. They managed to bring the arsenic level they measured in groundwater between 44.96 and 219.04 μg/L to drinkable levels by adsorption (100).

A similar study was conducted by Saha and Sarkar. In this study, an arsenic adsorbent consisting of alumina nanoparticles dispersed in a polymer matrix was developed and its arsenic adsorption properties were examined. In the study, the arsenic removal mechanism with alumina-loaded polymer beads was governed by both electrostatic adsorption and complexation. When As(V) removal is optimum at pH 7.2, the free amino group ($-NH_2$) in alumina nanoparticle dispersed chitosan-graftpolyacrylamide (CTS-g-PA) can exist in equilibrium with the protonated amino group in acidic aqueous solution.

Therefore, arsenate ions can interact with the polymer through electrostatic interactions / complexation (protonated amino group) and hydrogen bonds (unprotonated amino group). The positively charged Al^{3+} on the surface of the biosorbent will attract the negatively charged $HAsO_4$/H_2AsO_4 through electrostatic attraction. The maximum adsorption capacity of the nano-alumina loaded CTS-g-PA adsorbent prepared in batch studies was reported as 6.56 mg/g (35).

The most important disadvantages of nanoadsorbents are their high production costs, the difficult and costly separation of these very small adsorbents from the adsorption medium after the adsorption process, and their escape back into the treated water medium (33, 41, 42). In the current literature, there are various methods reported for the separation of nanoparticles after the adsorption process, such as magnetic separation, filtration and centrifugation method (41, 43, 44). Centrifugal separation of nanoparticles has been found to be a more effective method for non-magnetic nanoparticles due to its high efficiency, scalable production ability, lack of nanoparticle aggregation, and high density (43). In general, a centrifuge with a speed of 20,000-50,000 rpm has the capacity to remove nanoparticles from water (45-47).

External magnetic field and membrane filtration methods are frequently used to separate nanoparticles from aqueous solution (30). In particular, magnetic nanoadsorbent can be easily removed from the adsorption medium by applying a high magnetic field from outside. Separation by filtration has been done by various researchers using a 0.45 μm membrane filter. Considering the size and type of membranes, the filtration process has been chosen by many researchers to separate nanoparticles (48).

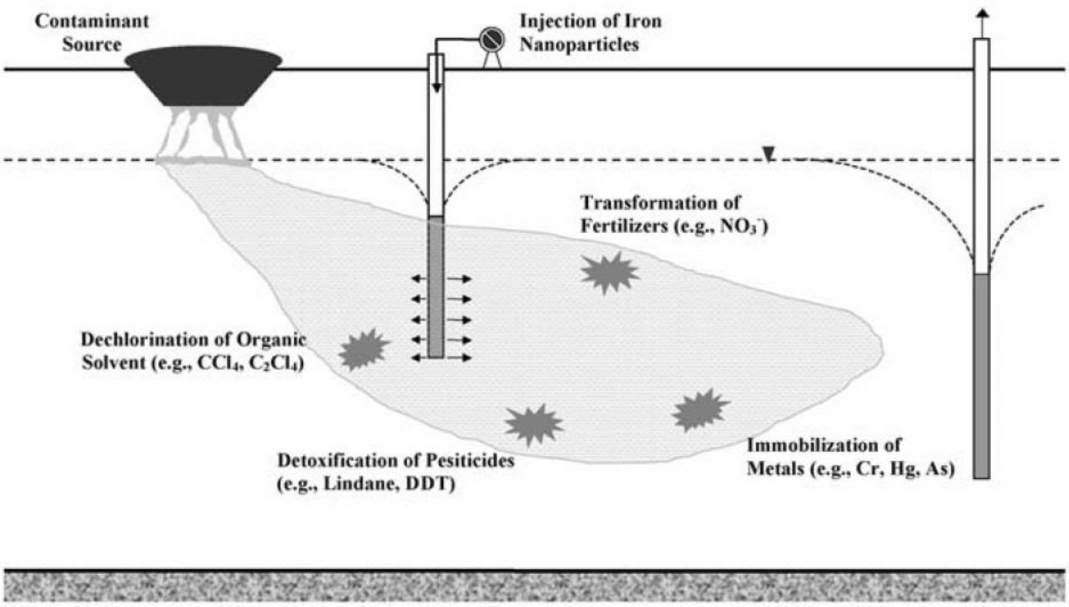

Figure 9: In-situ adsorption and magnetic separation. Figure republished with permission from Ref. (49).

Research has been conducted on in-situ applications as well as process applications for arsenic removal with nanoparticles. For example, nanoparticles can be easily used in sludge reactors to treat contaminated soils, sediments, and solid waste. Alternatively, nanoparticles can be attached to a solid matrix such as activated carbon and/or zeolite for improved treatment of water, wastewater, or gaseous process streams. Direct subsurface injection under gravity-fed or pressurized conditions has been shown to effectively transform chlorinated organic compounds (49).

However, nanoparticles without a stabilizer or surface modifier tend to rapidly aggregate into micron-scale or larger aggregates. As a result, the specific surface area and arsenic adsorption capacity of the adsorbent are greatly reduced. Therefore, to prevent the agglomeration of nanoparticles, stabilizers such as starch and carboxymethyl cellulose have been found to be effective in facilitating the size control of various metal and metal oxide-based nanoparticles (50).

4. NEW GENERATION DIFFERENT NANO ADSORBENTS FOR ARSENIC REMOVAL

Nanoparticles can generally be classified according to their chemical properties as organic (carbon-based), inorganic and composite. The most common inorganic nanoparticles used in water treatment are transition metal and metal oxide-based nanoparticles. These generally consist of Fe, Al, Ti, Si, Cu, Co, Zr, Ag and Zn and their oxides. Organic nanoadsorbents are classified as carbon nanotubes, graphene/graphene oxides, dendrimers and polymers due to their different shapes and chemical properties (31, 32). In order to benefit from the superior properties of inorganic nanoadsorbents such as mag-netism, composite nanoadsorbents have been syn-thesized through surface functionalization processes. For this purpose, composite nanoadsorbents have been created by coating metal oxides such as Fe_3O_4 with polymer or by functionalizing them with organic molecules such as $-NH_2$, -COOH or -

SO_3H on the surface, and positive results have been reported in water purification studies such as arsenic removal (33, 34).

These nanoadsorbents, nanospheres, nanotubes, nanowires and nanorods, prepared in various forms, have larger surface areas and allow high-capacity adsorption to remove arsenic ions from water.

According to literature nanoparticles used in water treatment should offer a high adsorption capacity and the used products should be easily separated from water and should not cause any harmful effects on the treated water. The fact that adsorbents are regenerable makes the adsorption process economically feasible. pH has an important role in the regeneration of adsorbents (30-32).

Criteria for ideal nanoadsorbent materials for water and wastewater remediation purposes are described by many researchers in literature (27-34, 41-47):

1. Nanoadsorbent materials should be non-toxic.
2. Nanoadsorbent materials should have high adsorption capacities and high selectivity to remove low concentrations of contaminants.
3. The surface of nanoadsorbent materials should be easily reactivated. So, it must be regenerable.
4. Nanoadsorbents should be easily separated from the adsorption medium and should not cause leaching.

4.1. Inorganic Nanoadsorbents

4.1.1. Metal/Metal Oxides

Nano-sized metal/metal oxide nanoadsorbents used in arsenic removal have attracted attention and have become the most studied adsorbents due to reasons such as being economical, non-toxic, widely available in nature and environmentally friendly. In particular, transition metals and their oxides have been widely synthesized at nanoscales and studied in water treatment processes (32, 43, 51). The magnetic properties of metals such as Fe, Co and Ni and their oxides make it easier to remove the adsorbent from the medium, especially after the adsorption process. Iron and iron oxides, which are metal and metal oxide-based nanoadsorbents, have been widely used in the removal of arsenic and a lot of research has been done on them. Especially iron-based adsorbents, which are non-toxic, low-cost and easily accessible in large quantities, offer promising results for arsenic removal from water (43).

Alumina (Al_2O_3), one of the nano-sized metal oxides used to remove arsenic, occurs in natural soils and has many structural forms such as ɑ, β, ϒ, ɵ and χ. In traditional methods, ɑ-Al_2O_3 is used as a natural adsorbent with greater stability. Alumina, is a popular sorbent because it has interesting properties; for example thermal conductivity, compressive strength, corrosion resistance, and extremely high electrical insulation. Aluminum oxides are very important adsorbents in arsenic removal due to their various nanostructured properties and low cost (31, 32).

Studies in the literature have revealed the importance of Al_2O_3 nanoparticles in the removal of arsenic by adsorption. Patra et al. synthesized a mesoporous adsorbent by self-assembling Al_2O_3 nanoparticles with a maximum size of 10 nm. The adsorbent they synthesized had high surface areas (231–497 m^2/g). They managed to remove arsenic with 86% efficiency at pH: 6.0 from solutions with 100 ppb AsO_2 concentration (52). Ghosh et al. synthesized Al_2O_3 nanoparticles for arsenic removal from water. In the adsorption experiments carried out in the batch system at room temperature, the arsenic adsorption capacity from As(III) and As(V) solutions at 400 μg/L concentrations with the synthesized Al_2O_3 adsorbate was 693.76 μg/g for the As(III) ion and 743.84 μg/g for the As(V) ion. At these rates, removal efficiency of 87.69% and 93.91% for arsenite and arsenate was obtained at pH:6.8 (53).

Another metal oxide that has been studied in the removal of arsenic from water is copper oxide (CuO) nanoparticles. There are many studies in the literature on the removal of arsenic from water with copper oxide CuO nanoparticles. Martinson and Reddy tried to remove As(III) and As(V) ions from groundwater with the CuO nanoparticles. The synthesized nanoparticles have a diameter range of 12–18nm and a surface area of 85m^2/g. In the pH range of 6 and 10, the maximum adsorption was 26.9 mg/g for As(III) and 22.6 mg/g for As(V). In studies conducted in the presence of competitive ions, the sulfate and silicate ions in water did not affect As(V) adsorption, but reduced As(III) adsorption. In addition, it was observed that only the phosphate ion reduced the adsorption of arsenic (54). Goswami et al. measured the surface area of the CuO nanoparticles they prepared for arsenic adsorption as 52.11 m^2/g. In their experimental study, with an adsorbent dose of 1 g/L from arsenic solution at a concentration of 200 ppb, 100% adsorption was achieved within 300 min interaction time. at pHs where the surface of the adsorbent is deprotonated, that is, at basic pHs, while 75% As removal was achieved at acidic values below pH:8. In arsenic adsorption carried out in the presence of phosphate and sulfate ions, it was observed that phosphate ion reduced arsenic adsorption by 20% and sulfate ion reduced the adsorption of arsenic by 10% (55).

Titanium dioxide (TiO_2) nanoparticles have also been used as adsorbents in several studies to evaluate the adsorption potential for the removal of arsenic from drinking water. Due to the low toxicity, chemical stability, resistance to corrosion and low cost of titanium-based nanoparticles, TiO_2 is a widely used adsorbent in water or wastewater treatment, as well as a semiconductor photocatalyst in UV light or sunlight. TiO_2 nanoparticles degrade organic contaminants and inactivate pathogens (56). Jegadeesan et al. investigated the effect of nano-sized amorphous and crystalline TiO_2 nanoparticles on the adsorption behavior of As(III) and As(V) ions in amorphous or crystalline structure. In experimental studies, samples were centrifuged and filtered through 0.45 mm Nylon filters. In experimental studies, adsorption reached its maximum value in the neutral pH range: 7-8. As a result of X-ray absorption spectroscopic analysis, they observed that As(III) ion prefers the amorphous structure over crystal surfaces in adsorption. It was determined that As(V) ion was adsorbed more on crystal surfaces. It was observed that silicate and phosphate ions had a negative effect on arsenic adsorption (57). Deng et al. investigated arsenic ions adsorption with TiO_2 nanoparticles. H-Fe_3O_4 microspheres with a hollow porous structure were synthesized from Fe_3O_4 with a size of 280 nm. Then, they coated the hollow Fe_3O_4 magnetic microspheres they synthesized with TiO_2 and obtained mesopores on the surface. The surface area of the synthesized adsorbent was measured as 179.98 m^2/g. In experimental studies, the maximum adsorption capacity of the adsorbent was 18.22 mg/g for As(III) ion, while As(V) ion was 7.74 mg/g. Maximum adsorption values were reached at pH: 3.0 for the As(V) ion and in the pH:3-10 range for the As(III) ion (58).

Zinc oxide nanoparticles are among the metal oxides that have been studied in the removal of arsenic from water. Singh et al. used ZnO nanoparticles functionalized with acetic acid to remove arsenic from contaminated water. They measured the dimensions of the synthesized ZnO nanomaterials as a maximum 60 nm. They observed that nanoparticles prepared from zinc acetate removed arsenic from water more effectively than those prepared from zinc chloride, zinc nitrate, and zinc sulfate. They think that acetate ions on the surface of ZnO adsorb arsenic via an oxo-coordination mechanism. In the experimental studies, arsenic adsorption reached a plateau at the 15th minute and at pH:5.8, and they managed to remove 99.92% of the arsenic from the medium by adsorption. In addition, in leaching studies, they reported that ZnO dissolved at low pH with HCl added to the medium and dissolved as $AsCl_3$ (59). Additionally, Rehman et al. carried out studies on the removal of arsenic from groundwater with the ZnO nanoparticles they synthesized. The size range of the synthesized ZnO nanoparticles varies between 3.6 nm and 12.7 nm. Arsenic adsorption was maximum at pH values lower than 5.0 (60).

Zirconium oxide nanoparticles are among the metal oxides studied in the literature for arsenic removal. Cui et al. synthesized ZrO_2 nanospheres with an average size of 7 nm and a surface area of 98 m^2/g and carried out As(III) and As(V) adsorption studies in a fixed bed reactor. The synthesized ZrO nanoparticles were treated with powder agar and micron-sized spheres were obtained. They carried out continuous system work using fixed bed columns. They interacted the ZrO_2 spheres they synthesized, which are non-toxic, extremely stable and resistant to acid and alkali, with water containing 300 ppb arsenic in a fixed bed column system for 10 minutes. Thus, they managed to reduce the amount of arsenic in the medium below 10 ppb (61). Zheng et al. in their As(III) removal studies with zirconia nanoparticles synthesized in the 60 – 90 nm size range, they managed to adsorb As(III) ions at 1.85 mmol-As/g in the pH range of 8-9 without pre-oxidation. In studies investigating the effect of competitive ions on adsorption, the presence of humic acid or typical anions (e.g., fluoride, silicate, phosphate, and sulfate) did not have substantially negative effects on As(III) adsorption. However, the adsorption of As(III) was inhibited due to the presence of bicarbonate ions (62).

Iron-based nanoparticles are the most studied metal/oxide nanoadsorbents in arsenic removal compared to other metal/oxide nanoparticles. In addition to being a suitable adsorbent for arsenic removal, nZVI, an iron-based nanoparticle, has attracted attention because it is a strong reductant and shows promise in the elimination of many pollutants. In addition, the fact that iron oxides have magnetic properties and can be controlled by an external magnetic field has made them among the popular nanoadsorbents, and magnetic Fe_3O_4 has become the most studied adsorbent. Due to the importance of iron-based nanoadsorbents, they are examined under a separate subheading (63).

4.1.1.1 Iron Based Nanoparticles

Studies conducted in recent years have revealed that iron-based adsorbents, which are low-cost and easily accessible in large quantities, can be easily used in the removal of arsenic from water, as iron does not have any known toxicity. Studies in the literature have shown that iron-based adsorbents can be developed in various ways and can be used with high efficiency in removing arsenic species from water (30-341.43). Although iron-based nanoadsorbents consist of nZVI and iron oxides, in some cases they are also prepared from mixtures of iron and different metals. Iron-based nanoadsorbents are increasingly used to remove both organic and inorganic pollutants from water. In addition, iron-based nanoparticles especially provide opportunities for in situ treatment applications. In addition to the high surface areas of iron-based nanoadsorbents and their high affinity for arsenic ions, the easy magnetic separation of some iron nanoadsorbents such as magnetite (Fe_3O_4) and maghemite (γ-Fe_2O_3) has made them very popular adsorbents in arsenic treatment (64).

The low release of arsenic back into the medium after the adsorption process from iron compounds such as hematite, goethite, iron oxide coated materials and granular ferric hydroxide (GFR) makes them important. Except for the PO_4^{3-}, Cl^-, NO_3^-, SO_4^{2-} and CO_3^{2-} ions do not have serious negative effects on the arsenic adsorption capacities of iron-based adsorbents in arsenic removal studies. Some adsorbents, such as ferric hydroxide and zerovalent iron, have been produced on an industrial scale as commercial adsorbents (63-65).

4.1.1.2. Nanozerovalent iron (nZVI)

Zero-valent iron (nZVI) is elemental iron that has an oxidation state of 0 and is written as Fe^0. nZVI attracts attention due to its high stability, large surface area, non-toxicity, reducing ability and with high adsorption capacity. nZVI is prepared by reducing iron or iron salts with various reducing agents, primarily $NaBH_4$, and using suitable capping agents such as organic surfactants and stabilizers. In recent years, nZVI, in addition to being an effective reductant, has attracted attention for its ability to degrade or oxidize other organic pollutants by combining with H_2O_2. nZVI can form soluble Fe(II) ions by reducing dissolved inorganics in water and these ions can then be oxidized to Fe(III) ions (66, 67).

In many studies in the literature, it is seen that nZVI is used as a catalyst in the removal of heavy metal ions and the oxidation of oxidizable organic and inorganic impurities in wastewater. To prevent oxidation, nZVI particles are alloyed or doped with other metal atoms such as Ag and Cu (63). Alloyed metals prevent iron from corroding. Iron nanoparticles can also be stabilized by incorporating them into some polymeric matrices.

Recent studies show that nZVI is effective in removing arsenic from contaminated water. The basis of nZVI's arsenic removal mechanism is the corrosion of zero-valent iron in the medium. Essentially, in arsenic removal, when oxygenated water comes into contact with nZVI, nZVI corrodes and provides the formation of various by-products such as Fe^{II} and Fe^{III} hydroxides, which can oxidize and remove arsenic. It is generally accepted that arsenic removal by ZVI involves adsorption, reduction, surface precipitation, and co-precipitation with various iron corrosion products such as iron/ferric (hydr)oxides (63, 65, 66).

Aggregation is a major problem of iron-based nanoparticles, and to overcome this, various polymers (e.g., neutral or charged polysaccharides) and other coatings have been used to stabilize nZVI particles. nZVI is characterized by a high tendency to agglomerate in water, high mobility, lack of stability and low reduction specificity, and therefore should be used in conjunction with surface stabilizers such as chitosan, alginate, activated carbon and other porous structures (49, 67). Therefore, Mosaferi et al. carried out an adsorption study by stabilizing nZVI with iron starch and carboxymethylcellulose for arsenic removal. In this study, they prevented agglomeration with their application and reported that the adsorption capacity increased by 36.5% for As(V) and 30% for As(III) (50). Yin et al. they managed to remove As(V) by 99.9% and As(III) by more than 70.9% in groundwater at 100 µg/L arsenic concentration with the 48 ± 9 nm sized nZVI nanoparticles they synthesized. In a study investigating the effect of common ions on adsorption, they reported that phosphate and carbonate ions decreased the adsorption efficiency (68). Morgada et al. conducted a study to investigate the effect of humic acid and UV light on the removal of arsenic from water with commercial nZVI (NanoFe1) in the 5-15 nm size range and 63 m^2/g surface area. From experimental studies, they found that nZVI removed arsenic with 90% efficiency in 150 min of interaction, and humic acid reduced arsenic removal by 50% in the dark. In studies investigating the effect of UV light, adsorption experiments were carried out in the presence and absence of humic acid. As a result of the experiments, it was observed that UV light doubled the adsorption of arsenic and that almost all arsenic was removed in a humic acid medium in 4 hours (69).

4.1.1.3. Magnetic Nanoadsorbents

Magnetic nanoadsorbents are one of the most important advanced nanomaterials that combine the superior properties of magnetic separation and nanotechnology in removing impurities from water. Nanosized magnetic Fe_3O_4 are an important member of magnetic nanoabsorbents. Magnetic separation technique is preferred in environmental applications because magnetic adsorbents can be easily removed from the environment by externally applied magnetic field high gradient magnetic separation (HGMS) technique at the end of the adsorption process (43, 64).

In general, magnetic nanoparticles contain elements such as iron, nickel and cobalt and their oxides. Iron oxide-based nanoadsorbents are basically divided into three forms: These are iron nanoparticles such as magnetite (Fe_3O_4), maghemite (c-Fe_2O_3) and hematite (ɑ-Fe_2O_3). Additionally, these particles are environmentally friendly as they are biodegradable (70). Besides favorable magnetic properties, low toxicity and price, iron oxide nanoparticles exhibit high surface/volume ratios and have high adsorption capacity for the adsorption of toxic pollutants in water purification procedures when associated with their surface chemical modification capabilities (71). Separation of contaminant-loaded adsorbents from water has always been considered a major challenge in drinking water treatment processes. Separating pollutant-saturated adsorbents from reactors and distribution systems is important to prevent secondary environmental pollution through the disposal of these materials. Magnetite nanoparticles are promising adsorbents for the removal of arsenic due to their high adsorption capacity and easy separation from water under external magnetic field (63).

Magnetic nanoparticles have a relatively larger surface area, biocompatibility, chemical stability, minimal toxicity and easy dispersion ability. Therefore, magnetic nanoparticles are more reliable, convenient and cost-effective to apply in water treatment (43, 72).

Mamindy-Pajany et al. studied arsenate adsorption on goethite, hematite and magnetite and found that arsenic adsorption was related to the iron content of the adsorbents and the adsorption rate increased in the order goethite < hematite < magnetite < ZVI. Moreover, desorption experiments show that arsenic is strongly adsorbed onto hematite and ZVI. They reported that among adsorbents, hematite appears to be the most suitable for the removal of arsenate in the natural medium, as it is effective over wide pH and arsenic concentration ranges (70). Mayo et al. compared the arsenic ions adsorption capacity of the 12 nm sized magnetic Fe_3O_4 nanoparticles they synthesized and the commercial 300 nm sized magnetic Fe_3O_4, and observed an approximately 200-fold increase in the adsorption capacity, depending on the size. They carried out the adsorption experiments by applying an external magnetic field to columns filled with stainless-steel wool. In this study, carried out using a high gradient magnetic field column separator, 99,2% separation was achieved with 12 nm-sized bare Fe_3O_4 nanoparticles from an As(III) solution at a concentration of 500 µg/L, while 90.9% of 20 nm-sized and 24.9% of As(III) ions were removed with 300 nm-sized particles. Under the same conditions, they were able to remove As(V) ion as 98.4% with 12 nm particles, 96.5% with 20 nm particles, and 29.2% with 300 nm commercial nanoparticles (73).

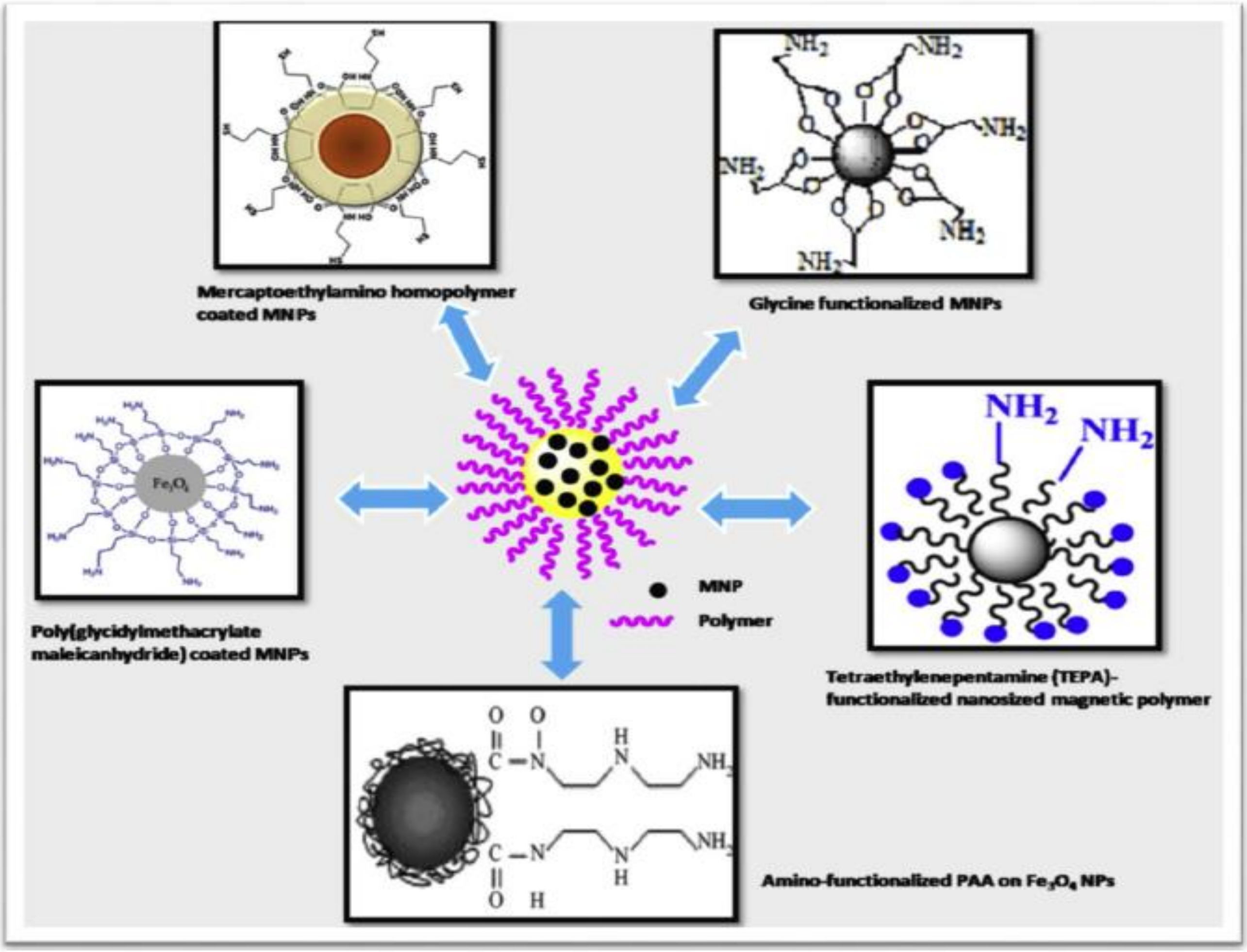

Figure 10: Surface functionalization of the of magnetic nanoparticles using polymers or organic molecules. Figure republished with permission from Ref. (43).

According to literature references, various adsorption forces such as electrostatic interactions, ion exchange and ion association tendencies, and complex formations play a role in the arsenic adsorption mechanism on the surfaces of oxide forms of iron. These properties of adsorbents play an important role in the affinity of pollutants to the surface of the adsorbent (63, 71-76).

4.1.1.4. Iron oxy-hydroxides

Many different materials have a high affinity for arsenic, but iron oxy-hydroxides are the most researched due to their easy accessibility. Commonly used iron oxy-hydroxides such as akaganeite (β-FeOOH), goethite (α-FeOOH), lepidocrosite (γ-FeOOH) and ferrihydrites ($Fe_{10}O_{14}(OH)_2$) can be chemically synthesized by precipitation of Fe(II) or Fe(III) salts through hydrolysis and oxidation processes (76).

Deliyanni et al. synthesized akaganeite with a nanocrystalline hybrid surface, which is an innovative adsorbent for the removal of arsenate ions from dilute solution. They observed that, unlike nanocrystalline akaganeite, the hybrid adsorbent prepared using cationic surfactant had a significantly higher arsenate adsorption capacity (approximately 180 mg As(V)/g) than pure akaganeite (approximately 120 mg As(V)/g) in the pH range of 4-10 (77).

4.1.2. Zeolite nanoadsorbents

Zeolites are aluminosilicate minerals with a surface structure containing numerous electrostatic holes occupied by cations and water molecules. Cations and water molecules have a significant choice of motion, allowing ion exchange and reversible dehydration. The normal size of zeolite is micro-scale, but nanozeolite can be produced in the range of 10-500 nm. Nano-scale zeolite has larger adsorption capacity, higher density of adsorption sites, and higher surface area (400-1000 m^2/g) than conventional zeolite (2, 27). Therefore, nano-zeolite has a great affinity and effective property against pollutants. It has been known since 1980 that zeolite is used together with silver (33).

Zeolites have been used extensively in separation and recovery processes for many years due to their highly porous structure. 1A and 2A group metal ions can be moved within their frameworks to balance the negatively charge between Si(IV) and Al(III). However, today, zeolites are used in the form of nanoparticles, which are more suitable for adsorption since they have a large surface area and therefore high adsorption capacity. (78). Attia et al. prepared a new zeolite (MNCZ) adsorbent coated with magnetic nanoparticle (γ-Fe_2O_3) to remove arsenic ions from aqueous solution. The results showed that MNCZ was effective in removing arsenic from aqueous solution, and the removal percentage of arsenic could reach over 95.6% within 15 min at pH 2.5. In this study, the adsorption capacity of MNCZ particles was reported to be 19.39 mg/g (78). Pizarro et al. studied arsenate removal from water with a composite adsorbent they synthesized from 50 nm magnetic Fe_3O_4 and zeolite. In this study, in which zeolite was used as support material; the maximum arsenate adsorption was 5.1 mg/g (37).

4.1.3. Silica-based nanoadsorbent

Nanosized silica oxides, which constitute another group of inorganic nanoadsorbents, have unique properties such as large surface area, controllable surface properties and well-defined pore size. Therefore, it has great potential in water treatment processes. In addition, nanosilica is an environmentally friendly adsorbent that has no toxic effects on health. In addition, adsorption capacity and selectivity can be increased by modification of their surfaces with functional groups such as $-NH_2$ and -SH. (79). Studies have shown that naturally occurring adsorbents such as iron-coated sand are cost-effective arsenic treatment technologies.

Jamali-Behnam et al. synthesized 100 nm-sized magnetic Fe_3O_4 nanoparticles to remove As(III) and coated these magnetic nanoparticles with silica. While magnetic nanoparticles tended to aggregate, such a behavior was not observed in silica-coated ones and they removed more than 99% of arsenic from the medium. The maximum adsorption was 33.36 μg/g for MNPs and 32.10 μg/g for Si-MNPs (80).

4.2. Organic (Carbon Based) Nanoadsorbents

Carbon-based functional materials are among the most important nanoadsorbents used in water treatment due to their distinctive physical and chemical properties and functionalizable surface properties. Carbon-based nanoadsorbents enable selective adsorption studies because their dimensions and surface properties can be adjusted, and they attract the attention of researchers due to these features. For a long time, research has been carried out to obtain various carbon-based nanoadsorbents such as graphene, activated carbon, carbon nanotubes, carbon-based nanocomposites and their derivatives for the removal of various types of pollutants from water (30, 31, 79).

Activated carbon is widely used today for the removal of metallic impurities. Activated carbons are of great interest in the removal of heavy metal ions from water due to their large surface area (27). Scientific research continues to obtain cheap and effective activated carbon from carbon-based materials and to use it in removing heavy metals from water. However, activated carbon poorly adsorbs arsenic species due to its negatively charged surface (81). For this reason, composites are prepared. Rodrigez et al. tested the ability of activated carbon modified with iron hydroxides to adsorb arsenic from water. They reported that activated carbon modified with FeOOH- which has a surface area of up to 1101 m^2 adsorbed As(V) up to a maximum of 1250 mμg/g in the range of pH: 6-8. In the study conducted on groundwater samples, they observed that adsorption decreased in the presence of Cl^-, SO_4^{2-} and F^- ions (81).

4.2.1. Carbon Nanotubes

Carbon nanotubes are carbon nanostructures with a cylindrical form. Based on the synthesis process, carbon nanotubes are classified as single-walled or multi-walled nanotubes. Carbon nanotubes due to their cylindrical hollow structure have higher surface area, electrical conductivity, high adsorption sites, and tunable surface chemistry. Carbon nanotubes are divided into two main groups: single-walled (SWCNTs) and multi-walled (MWCNTs) (82).

Carbon nanotubes can be applied to determine the preliminary concentration and reveal pollutants as it can be applied, especially, to remove organic pollutants. The interaction between carbon nanotubes and metal cations is achieved through electrostatic attraction and chemical bonding. In studies conducted in the literature, the mechanism of removing oil from wastewater using carbon nanotubes has been clearly explained. Although carbon nanotubes have significant advantages over activated carbon, using them to treat large amounts of wastewater on an industrial scale is currently not feasible due to high production costs. However, carbon nanotube application will be more competitive in the short term (2, 31).

Despite these positive properties of carbon nanotubes, the adsorption capacity of metal ions using raw carbon nanotubes is very low, but their adsorption capacity can be significantly increased after oxidation of carbon nanotubes using HNO_3, NaClO and $KMnO_4$ solutions. Carbon nanotubes in different forms (single-walled or multi-walled closed or open-ended CNTs) have been used for the removal of various contaminants (79). The modification technique of carbon nanotubes should be selected according to the contaminant. Metal oxide-modified materials combine the adsorption properties of metal oxides and the outstanding properties of carbon nanotubes, such as large surface area, evenly distributed pores, and the presence of functional groups on the surface (83).

The hydrophobic surface properties of carbon nanotubes cause stabilization through particle aggregation in aqueous solution to prevent decreases in surface activity. There are numerous reports regarding oxidation and surface modification (2, 27, 31, 32, 79). In addition to the fact that oxidation and surface modification processes provide carbon nanotubes with sufficient adsorption sites, carbon nanotubes also serve as a good support material for other adsorbents.

Imran Ali carried out As(III) and As(V) removal studies with multi-walled carbon nanotubes (MWCNTs) that he synthesized with dimensions of 10–40 nm and a surface area of 9.1 m^2/g. He carried out adsorption studies at pH: 6.0 at a concentration of 40 μg/L and managed to remove As(III) with 91% efficiency and As(V) with 92% efficiency. He also carried out experimental studies as batch and column studies. He carried out experimental studies separately as batch and column studies. One of the two 25 cm long glass columns, separated by a glass filter with 20 μm pore size, was filled with carbon nanotubes and the other was filled with river sand and treated with arsenic water with the help of a peristaltic pump at a flow rate of 45 min per minute. In experimental studies, maximum adsorption occurred at pH 6.0, 92.0% for As(V) and 91.5% for As(III). Additionally, from column studies, the capacity of the adsorbent to remove arsenic ions was determined as 13.5 μg/g for As(III) and 14.0 μg/g for As(V) (84).

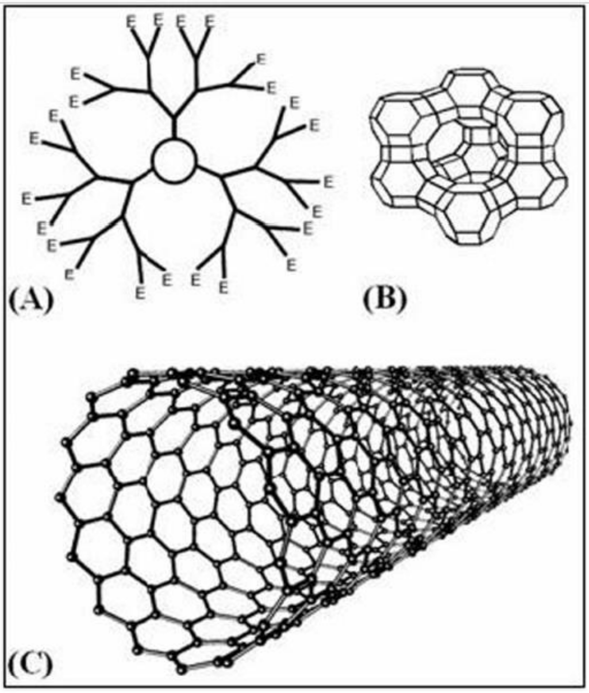

Figure 11: Nanosorbents structures for adsorption processes: (A) dendrimer, (B) zeolite and (C) carbon nanotube. Figure republished with permission from Ref. (79).

4.2.2. Graphene/graphene oxide nanomaterials

Graphene (G) and graphene oxide (GO) have attracted great attention since the discovery of graphene. Graphene and graphene-based nanoadsorbents have been prepared and used for the removal of pollutants in water, including metal ions and organic compounds. Graphene, another member of carbon-based nanoadsorbents, has received significant attention especially in the field of water remediation. Graphite oxides can be easily synthesized on a large scale from low-cost natural graphite. Additionally, graphite oxide is much more applicable than pure graphite, as hybrid multifunctional materials can be synthesized with iron-based nanoadsorbents (28).

The presence of oxygen-containing functional moieties on the surface of graphene oxide provides it with a strong hydrophilic structure, and this leads to its dispersion in water. Graphene oxide can be used effectively in wastewater treatment processes due to its high surface area as well as the functional groups it has on its surface. These nanoadsorbents are preferred in the removal of various pollutants in wastewater. Removal of heavy metal ions by adsorption occurs through complexation with the oxide binding site in graphene (79). Tabatabaiee Bafrooee et al. (2021) modified the surface of the adsorbent they prepared with EDA by embedding magnetic Fe_3O_4 between the GO layers they synthesized to remove As(III) from water. The As(III) removal capacity of the functionalized magnetic graphene oxide composite adsorbent they prepared was 13.3 mg/g. They reported that at 10 mg/L arsenic concentration, As(III) adsorption occurred as 60% in the first 5 minutes, and removal occurred with 80% efficiency at pH:8.0 by forming a complex on the adsorbent surface (85).

4.2.3. Polymeric nanoadsorbents

In recent years, polymeric adsorbents have emerged as alternatives to traditional adsorbents in terms of their large surface area, tunable surface chemistry, excellent mechanical properties, adjustability of dimensions, applicability under harsh conditions and allowing regeneration (86). Polymer-based nanoadsorbents are preferred for the selective removal of impurities due to the hydroxyl, amine, amide and carboxyl functional groups on their surfaces. Specific interactions between functional groups attached to polymeric matrices and the target ion are effective in the adsorption capacity and selectivity of synthetic polymers against metal ions (29). In removing arsenic from water, the redox structures of these materials, their adsorption abilities, and their tendency to form complexes and/or precipitate against various pollutants should be taken into consideration.

The low surface area and slow adsorption rate of conventional adsorbents pose a limitation to their applications. Meanwhile, metal/metal oxide nanoparticles have large surface area, but lack functional groups on their surface to chelate metal ions. The development and application of polymer-based nanoadsorbents and nanocomposites provide an alternative opportunity for effective removal of impurities in water (30, 79). As nanoadsorbents, polymeric nanoparticles and polymer-supported nanocomposites, metal/oxide nanoadsorbents have large surface areas and multifunctional groups on the surface compared to other adsorbents.

Polymers are also used especially in surface modification to obtain selective and higher adsorption capacities of magnetic nanoparticles. In addition, polymeric coating provides important advantages to nanoparticles such as chemical stability, mechanical strength and biocompatibility (31, 32). Polymeric nanoadsorbents can generally be prepared in the form of spheres or membranes. Nanofibrous membranes have become preferred in membrane systems due to their well-defined porous structures, higher permeability, small interfiber pore sizes and large surface areas. They have high strength, tunable surface functional groups and the ability to be easily degraded. These features make them an excellent choice among adsorbents. The adsorption process on the polymeric membrane surface composed of nanofibers involves the retention of metal ions by functional groups on the membrane surface and the penetration of wastewater through the membrane (86). The presence of special functional groups such as $-NH_2$, $-COOH$, $-SO_3H$ etc. in polymers can be achieved by the use of different monomers or surface modification while synthesizing the polymer. These groups that the polymer has determine the adsorption capacity and selectivity of the nanoadsorbent (2, 31, 32). Spherical polymeric nanoparticles among polymeric nanoadsorbents can be prepared in different forms such as polymer nanofibers, polymer nanocrystals and polymer nanorods. Polymer-based nanoadsorbents can be categorized as biobased or synthetic on the material used. Synthetic organic polymers or biopolymers, namely cellulose, alginate and chitosan, carrying multifunctional groups such as $-NH_2$, -SH, –OH, –COOH etc. on the surface, are used to effectively adsorb arsenic ions in water (79).

4.2.4. Chitosan nanoadsorbents

Chitosan is a hydrophilic, biocompatible, non-toxic, environmentally friendly polymer that can form complexes with metal ions with its amino and hydroxyl groups. Adsorption on chitosan occurs not only electrostatically with the functional groups on the surface, which can be charged depending on the pH of the environment, but also by interaction with metal ions through chelation. In addition. the functionalization process for adsorption efficiency and selectivity also stabilizes chitosan in an acidic environment and increases its mechanical properties (87, 88).

Min et al. synthesized Fe-doped chitosan electrospun nanofibers to remove As(V) from water. They reported that the maximum As(V) adsorption of the chitosan nanofiber they synthesized with a diameter of 128 nm to 153 nm was 11.2 mg/g at pH 7.2. In their XPS and FTIR analyses, they observed that –NH, -OH and C-O functional groups in the structure of chitosan were effective in As(V) adsorption. Additionally, in examining the effect of other ions on adsorption, they reported that while arsenic adsorption decreased with increasing solution ionic strength, Cl^- and SO_4^{2-} anions up to 1 mM did not affect the adsorption of arsenate, but SiO_3^{2-} and PO_4^{2-} ions had a significant negative effect on adsorption (89).

4.2.5. Cellulose-based nanoadsorbents

Dendrimers are organic polymeric adsorbents containing high amounts of chelating amine functional groups and are a nanomaterial that is being researched for metal adsorption. These adsorbents provide advantages because they are based on natural cellulose, are non-toxic and economical (28).

Chaia et al. carried out an arsenic removal study with pH-sensitive nanocellulose-based nanoparticles that they synthesized by using polyethyleneimine and glutaraldehyde as cross-linkers. With the cellulose nanoparticles they synthesized, they managed to quickly adsorb As(V) ions at a maximum capacity of 255.19 mg/g in acidic conditions, especially at pH: 3.0. Then, they could easily regenerate the adsorbent using NaOH (90).

4.2.6. Dendrimer nanoadsorbent

Dendrimers are organic polymeric adsorbents containing highly chelating amine functional groups and another potential nanomaterial for metal adsorption. Typically, dendrimers are symmetrical around the core and often have a spherical three-dimensional morphology. Dendrimers, which have repeatedly branched molecules, are considered an excellent example for their effectiveness in removing organic and inorganic pollutants. The general properties of dendrimers are determined by the functional groups they have on their surface, but there are also examples of dendrimers with functionality within the structure (28, 31, 91).

Prabu et al. synthesized graphene oxide-polyamidoamine dendrimer (up to 2nd generation, (GO-gen2) adsorbents) by the grafting method to remove As(V). They then functionalized the surface of the adsorbent with aromatic triazine rings which is rich in aromatic nitrogen. They entrapped ZrO in this synthesized adsorbent and examined its adsorption behavior of AsO_3 ion from water. The maximum adsorption capacity of the dendrimer composite adsorbent in GO sheet form was 1.075 mmol/g for AsO_3 (91). Yavari et al evaluated the effect of polyamidoamine dendrimer generation 3 (PAMAM G3) as an adsorbent in the removal of As(V) from aqueous solutions. They carried out their experimental studies in the pH range of 2-10 and the maximum adsorption was 233.17 mg/g at a concentration of 1000 mg/L at pH:7.0. They reported that the adsorption mechanism occurs through the electrostatic interaction of negatively charged arsenic ions with the positively charged dendrimer surface at pH = 7.0 (92).

4.3. Composite Nanoadsorbents

Each of the organic and inorganic adsorbents used in the removal of toxic pollutants from water has superior properties but also shortcomings. Although metal/metal oxide nanoadsorbents are natural and inexpensive, they have disadvantages such as specificity, stability and aggregation. Despite their superior properties such as having different functional groups that allow interactions on their surfaces and being regenerable, organic adsorbents have disadvantages such as being relatively expensive to synthesize compared to inorganic ones, difficult to remove from adsorption medium and costly to use. Researchers have focused on developing new composite adsorbents that have the superior properties of organic and inorganic adsorbents. Researchers have carried out studies to develop composite adsorbents with superior properties by combining the superior properties of carbon-based adsorbents, such as allowing the physico-chemical properties of the adsorbent used to be modified and maintaining its stability under harsh conditions, and the superior properties of magnetic adsorbents, such as being easy to separate because they are natural, economical and magnetic. In this way, the tendency of inorganic adsorbents to form aggregates can be prevented. In addition, the leakage of metals into the adsorption medium is prevented (93). There are studies in the literature to remove arsenic from water with various composites consisting of carbon nanotubes, graphene oxide, activated carbons and iron oxide nanoparticles (41, 43). In addition to this approach, there are many studies on arsenic removal from water with composite nanoadsorbents embedded in polymeric nanoadsorbents. Composite studies, in particular, where magnetic properties are utilized and Fe_3O_4 nanoparticles are surface modified with molecules having functional groups such as $-NH_2$ -COOH or $-SO_3H$, are among the areas where researchers focus on (31).

4.3.1. Organic polymer supported nanocomposites

Magnetic nanoparticles, which are the most common inorganic nanoadsorbent used in arsenic treatment, can be prepared as composites by coating them with polymers, embedding them in the polymeric structure, or bonding organic molecules to their surfaces. In addition to the important developments in the synthesis of magnetic nanoadsorbents, preserving their stability by preventing their agglomeration and precipitation is also an important issue. To overcome these shortcomings, bare magnetic nanoparticles can be functionalized with different molecules. Surface modification of magnetic nanoparticles increases the selectivity and adsorption capacity towards certain metal ion, as well as increases the stability of magnetic Fe_3O_4 against oxidation (79).

In functionalization, polymeric coating using polyethylene glycol (PEG), polyvinyl alcohol (PVA) and polyvinylpyrrolidine (PVP), etc., provides complex formation, chemical bonding and ligand combination in addition to the electrostatic and Van der Waals interactions responsible for metal ion adsorption on the adsorbent surface of magnetic nanoparticles. Thanks to coating polymers, agglomeration of magnetic nanoparticles can be prevented (41).

This process provides a larger surface area/volume ratio and promotes better dispersion of magnetic nanoparticles in solution. Functionalization of the surfaces of magnetic nanoparticles allows specific adsorption of metal ions. In addition to coating magnetic nanoparticles with polymers, many studies have also been conducted on functionalizing them with biological molecules or functional molecules (71-76).

Polymeric nanocomposites are also categorized in terms of the incorporation of inorganic nanoparticles into a polymer matrix. Organic polymer-supported nanocomposites are formed by preparing organic polymers together with inorganic nanoadsorbents such as $Fe/TiO_2/Fe_3O_4$. Polymers covering the surfaces of metallic nanoadsorbents can be examined under two different groups: synthetic polymer-supported nanocomposites and biopolymer-supported nanocomposites. The first group includes synthetic polymers such as polyaniline (PAN), polystyrene, polyhydroxybutyrate (PHB), poly(tetrafluoroethylene), polyethylene (PE), and nafion. Biopolymer-supported nanocomposites are prepared with biological polymers such as cellulose, chitosan and alginate or resin (31).

Türkmen et al. embedded the nano-sized Fe_3O_4 magnetic nanoparticles they synthesized into the polymer to remove arsenic. They synthesized polymeric nanoparticles with the –SH functional group on their surface using the molecular imprinting technique. With the nanoparticles they synthesized, they managed to adsorb the As(III) ion as 76.83 mg/g nanoparticles and the As(V) ion as 87.57 mg/g nanoparticles at pH: 5.0. It can be seen from SEM analysis that the sizes of the magnetic Fe_3O_4 containing nanoparticles they synthesized are in the range of 30-40 nm (94).

Metal oxide nanoadsorbents have a tendency to aggregate, which causes a decrease in their surface area and, as a result, a decrease in adsorption capacity is observed. However, adsorption capacities can be increased by functionalizing them with polymers and preparing their composites. However, modification of the metal oxide surface contributes to both increasing the adsorption capacity of the nanoadsorbent and increasing its selectivity. In particular, the oxidation tendencies of iron nanoparticles can also be controlled by alloying it with another stable metal or coating them with some polymers.

Alginate, a biopolymer, has also been applied as a biopolymer support in the construction of nanocomposites to remove toxic elements from water. Haris et al. carried out an As(III) removal study with the 12 nm-size bare and alginate encapsulated super paramagnetic nanoparticles they synthesized. The dimensions of the alginate-coated and bare super paramagnetic nanoparticles were 25-30 nm and the maximum adsorption occurred at pH:7.0. They succeeded in removing 90% of arsenic from the solution at 6.5 mg/L As(III) concentration with bare iron oxide nanoparticles and 99% with alginate-coated ones (95). Chitosan nanoparticles have faster adsorption rates and higher adsorption capacities compared to micro-chitosan materials. Abdollahi et al. synthesized chitosan nanoparticles containing magnetic Fe_3O_4 to remove arsenic from water. They determined that chitosan-coated nanoparticles were 10 nm in size. They reported that the adsorption behavior obeyed the Langmuir adsorption isotherm model and reached a maximum of 10.5 mg/g at pH: 9.0. They also reported that at 10 mg/L As(III) concentration, As(III) ion adsorption was 74.59 mg/g for bare Fe_3O_4 nanoparticles and 87.46 mg/g for Chitosan-coated Fe_3O_4 nanoparticles (96).

4.3.2. Nanoparticles functionalized with organic/biomolecules

Functionalization of magnetic nanoadsorbents with organic/biomolecules not only increases the adsorption capacity, but also enables their safe and environmentally friendly use in the purification process of metal ions. Many researchers have investigated the use of magnetic nanoadsorbents functionalized with biomolecules in the adsorption of heavy metals as well as arsenic ions. Functional groups on the surfaces of nanoparticles whose surfaces are functionalized with organic molecules greatly increase the adsorption capacity and also provide selectivity to inorganic nanoadsorbents by forming complexes with metal ions (31, 41, 42, 97).

Tripathy et al. functionalized the surfaces of the Fe_3O_4 magnetic nanoparticles they synthesized with L-cysteine (an amino acid). Thus, they developed a dispersible adsorbent that can be collected magnetically. Later, they used this adsorbent to remove As(III) and As(V) ions from water. They reported that the cystein-functionalized mesoporous magnetic Fe_3O_4 nanoparticles they synthesized adsorbed 20.0 mg/g As(III) and 34.0 mg/g As(V) ions. In their studies, they managed to adsorb approximately 93% of As(III) (at pH: 7.0 and 9.0) and 95% of As(V) (at pH: 5:0) onto the surface of Fe_3O_4-cysteine. Functionalizing the surface with L-cysteine not only increased the dispersibility of Fe_3O_4 nanoparticles in aqueous suspensions, but also effectively prevented iron ions from leaking into the solution (98).

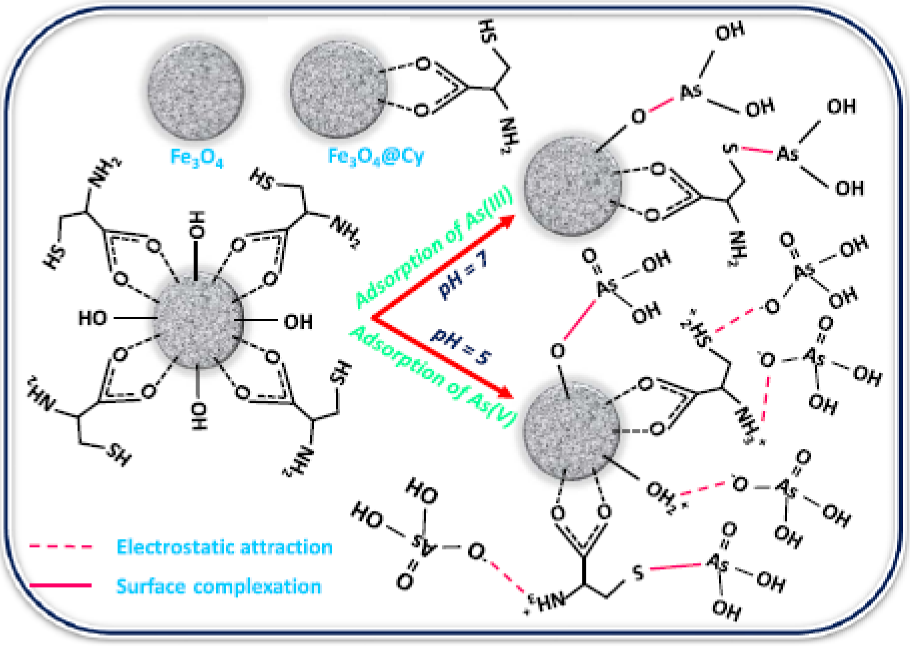

Figure 12: Schematic representation of the arsenic ions adsorption mechanism of Fe_3O_4 nanoparticles functionalized with cysteine. Figure republished with permission from Ref. (98).

5. FACTORS AFFECTING ARSENIC ADSORPTION

The most important parameter in metal adsorption studies is the ambient pH. In metal adsorption processes, at low pH, electrostatic repulsions between protonated functional parts and metal cations on the surface of the adsorbents cause a decrease in adsorption. In addition, H^+ and H_3O^+ ions, which increase in the medium due to the decrease in pH, compete with metal cations in adsorption. However, at intermediate pH values, the amount of adsorption increases due to the decrease in electrostatic repulsion due to deprotonation of functional groups. We can state that medium pH is suitable for the removal of toxic metal ions because in this case the adsorbent surface is deprotonated, which causes an increase in negatively charged regions. This causes increased electrostatic attractions between the adsorbent surface and metal cations, leading to an increase in adsorption capacity. In basic conditions, hydroxylated complexes of metal ions in the medium are formed (42, 74, 93).

The situation here is slightly different in removing arsenic from water. In aqueous media, As(III) and As(V) ions exist in the form of oxyanions and vary depending on the pH of the medium. As the pH of the medium increases, the negative charge value of As(V) ions in the negatively charged oxyanion form increases, but in acidic media, the uncharged As(III) form turns into a negatively charged form after pH: 9.0. At pH values below 9.0, where it is uncharged, arsenite ions can be removed from the medium by complexing with the adsorbent rather than electrostatic interactions (32, 43).

Another parameter that affects adsorption is the dose amount of the adsorbent. As the adsorbent dose amount of nanoparticles in the medium increases, the adsorption capacity increases. However, the high amount of adsorbent added to the medium causes the nanoadsorbents to form aggregates, which leads to a decrease in the surface area and a decrease in adsorption, and therefore a decrease in the adsorption capacity (43, 79).

Another factor affecting adsorption is metal ion concentration. The adsorption rate increases with the increase of metal ion concentration to a certain degree at the beginning, but more increase causes the removal efficiency to decrease. This may be because the optimum metal ion concentration must be present in the solution for a certain amount of adsorbent. The presence of a low concentration of metal ions in the medium means fewer metal ions available for adsorption, leading to a low removal rate, but if the concentration increases, it causes an increase in the amount of ions available for adsorption and an increase in the interaction with the binding sites, resulting in a higher adsorption rate (28).

Especially in metal ion adsorption on large scales, the contact time between metal ions in solution and adsorbents is important and time plays an important role in economical wastewater treatment processes. Since it is easier for analyte ions to access the active areas of nano-sized adsorbents with high surface areas, reaching equilibrium in adsorption occurs in a shorter time and thus maximum adsorption capacities are reached in a short time (32, 75).

Another point that affects the adsorption is the temperature of the adsorption medium. Adsorption medium temperature is also an important parameter in the adsorption process. In general, the increase in initial temperature reduces the viscosity of the solution, resulting in increased diffusion rate of the analyte across the adsorbent surface, leading to higher adsorption efficiency. Adsorption phenomenon is an exothermic phenomenon and as the temperature increases, the kinetic energy of the analyte increases and adsorption decreases. The change in temperature affects adsorption in two different ways, depending on whether the system exhibits heat absorption or heat dissipation behavior. In an exothermic process, the adsorption capacity decreases with increasing temperature, while in an endothermic process it increases (72).

Ion diversity in the medium also affects adsorption. Especially, depending on the affinity of the functional groups on the adsorbent surface to the target metal ion, the adsorption of the target ion is affected by the presence of competitive ions in the medium. Since competing ions in the medium occupy active sites by creating chelation on the surface, there is a decrease in the adsorption of the target metal ion. In addition, for selective adsorption, it is necessary to specifically design the adsorbent surface or use selectivity-oriented techniques such as molecular imprinting (29, 94). During arsenic removal processes from water, the presence of anions such as PO_4^{3-}, Cl^-, NO_3^-, SO_4^{2-} and CO_3^{2-} ions in the medium affects the adsorption of arsenate and arsenite ions, which are in the form of negatively charged oxyanions. Studies in the literature have reported that especially the PO_4^{3-}ion significantly affects adsorption (43, 65).

6. CONCLUSION

In recent years, developments in nanoscience and nanotechnology have enabled the development of efficient, economical and environmentally friendly approaches to environmental remediation. Nowadays, nanomaterials as adsorbents with large specific surface area, functionalized surfaces for more and selective adsorption, and less tendency to agglomerate have attracted great attention in the decontamination of water. Particularly prepared nanocomposites have become promising adsorbents for water treatment due to their physicochemical properties (34).

Scientists have extensively reported studies on various nanostructured materials such as metal/metal oxide, carbon-based and composite materials used as adsorbents in the removal of heavy metal ions. Moreover, recent literature searches show that research focuses on surface functionalization and modification of adsorbents for their better dispersion and easy separation in the adsorption medium. To improve their surface properties of nanoadsorbents in the functionalization different molecules such as inorganic, organic, polymeric, biomolecules, etc. are used (31, 44).

Research and adaptation studies for the treatment of arsenic from water continue at both laboratory and industrial scales. However, the instability of some nanoadsorbents and the difficulty of removing them from purified water and regenerating them have limited their commercial use. The biggest disadvantage of using nanosized adsorbents is the high cost (49, 65). In addition to the fact that there are difficulties in removing nanoadsorbents from the adsorption medium, another disadvantage is that the toxic effects of toxic metal-loaded nanoadsorbents remaining in the medium have not been clearly elucidated.

Considering the various studies reported so far, it is concluded that composite magnetic nanoparticles may be a better option for removing arsenic from waters. In the selection of nano adsorbents for arsenic removal, factors such as adsorption potential, high surface area, physical and chemical stability, ease of production and applicability, solubility product of the adsorbent, easy separation of the adsorbent from water, leachability to the water medium, its toxic effect, cost and regenerability and in-situ applicability should be taken into consideration (30, 63, 65, 75, 99).

Although nanoadsorbents have unique properties, most of the adsorption studies are at laboratory scale and their industrial applications are quite few. Laboratory studies by the scientists to develop nanoadsorbents with desired properties and suitable for use in industrial systems are still continuing. Researchers have concerns due to the uncertainties about the health problems that nanoadsorbents may cause due to problems in their recovery from the medium (33). Detailed studies on the design and development, surface modification and applications of new generation adsorbents are continuing intensively, and these adsorbents are promising in environmental applications and water treatment. The use of nanoparticles for water purification at laboratory scale has shown promising results, but further improvement of their physicochemical properties appears to be needed for full-scale application (44, 49).

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