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Mitigation Techniques of Arsenic in Groundwater and its Sustainable Use

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Abstract: **Arsenic is one of the major groundwater contaminants in different parts of the globe. The major source of As in groundwater is geogenic processes. A large population on the globe is depends on groundwater for drinking and domestic purposes. Contamination of As imposes severe health consequences on the human health. Prolong exposure of As causes arsenocosis. So proper monitoring and the treatment of groundwater before human use is very much required. In the current review an endeavor has been made to recognize the kinetics and geochemistry of As in the aquifers. Different mitigation strategies of Arsenic removal from the groundwater are discussed in this paper. Different remedial measures like adsorption, oxidation, ion exchange, membrane process and phytoremediation of As contamination are described briefly.**

Index Terms: **Enter at least 5 key words or phrases in alphabetical order, separated by commas. (Times New Roman, Font Size 9, Bold)**

I. Introduction

A severe and dangerous health hazard has occurred in human beings due to toxic contaminants and harmful pollutants present in the atmosphere. Heavy metal contamination is the utmost lethal and detrimental contaminant. These heavy metals are present everywhere and deadly toxicants despite their persistent nature. Heavy metals are present in abundant amount, and it is devoid of biodegradable capacity. These heavy metals have contaminated the groundwater on a vital range in different parts of the world. Arsenic (As) is one of the lethal and harmful pollutants worldwide (Stopelli, 2020). This is spread on a wide range due to its production by various natural and anthropogenic actions. These activities include various agricultural activities along with mining and industry action. Heavy metals are more prone to cancer and other severe diseases in human beings. Groundwater contaminated with arsenic is a serious concern regarding ecology as well as health. As groundwater is the primary source to fulfill the drinking and irrigation needs of people (Saha and Ray, 2019; Suhag, 2019). Arsenic contamination has spread in various parts of the world. These regions include the south and south-east Asia, India, China, and Bangladesh. (Fendorf et al., 2010; Rodriguez -Lado et al., 2013). The range of contamination in these places is up to 3000 µg L-1 As. This range is much higher than the threshold value (10 µg L-1) given by World Health Organization (WHO) (Smedley and Kinniburgh, 2002; Rahman et al., 2020). Groundwater is used for several purposes, including drinking and irrigation. Among various uses, these two are considered as most essential for health issues. Contaminated groundwater with arsenic, when used for irrigation, affects the crops with arsenic contamination and can cause accumulation of arsenic in the crops like cereals or pulses. As a result, the food crops irrigated with contaminated water deteriorate the health of human beings and cause various diseases (Senanayake and Mukherji, 2014). As we know that freshwater is available only in limited quantity, the contamination must be reduced. According to WHO 1993 (WHO, 1993), the permissible limit for drinking water in arsenic contamination is 10 ug L^{-1}. The remediation process of arsenic-contaminated water includes various traditional approaches like coagulation-flocculation, adsorption, precipitation, ion exchange, and microbial. The techniques related to arsenic mitigation require the oxidation of arsenite to arsenate. Arsenite (As III) is the most dominant molecule, H_3AsO_3 found in

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groundwater. At the same time, arsenate (As V) exists as anionic species (H_2AsO^{4-} or $HAsO_4$). The long-term consumption of such arsenic-contaminated groundwater (5 to 10 years) either as drinking water or food can be a reason for arsenecosis. Arsenecosis deals with several health-related problems like skin disorders, skin cancers, internal organ cancer; it may be bladder, lungs, or kidney. Arsenecosis causes disease of blood vessels, limbs, and feet. It may be a reason for diabetes or blood pressure. As may induce problems related to reproductive issues.

A. Arsenic Contamination in Groundwater: An Overview

In India, Over 50 million people are suffering from the threat of arsenic contamination. Various researchers are involved in groundwater contaminated with arsenic, particularly the Ganga basin (Chakraborti et al., 2018). River Ganga is the most fertile area and is covered with densely populated regions (Khan et al., 2016). At present, River Ganga is a highly polluted river and contaminated with various heavy metals like arsenic, chromium, copper, cadmium, lead, mercury. Along with toxic and hazardous pesticides and harmful microbes. These harmful microbes and pesticides have crossed the safe limits of the permissible value (Tandon, 2018).

Contamination of harmful and toxic heavy metal arsenic can be easily boomed devastative in groundwater. The presence of rock water with the aqueous resources is the main reason for the contamination of arsenic in groundwater. Arsenic is a highly toxic element and known as the King of poison (Shaji et al., 2020). Mobilization of arsenic occurs in groundwater systems due to hydraulic fracturing. After contaminating the groundwater reservoir, many people can be affected (Murcott, 2012). More than seventy countries are affected due to the wide range of arsenic contamination in the groundwater. This range may vary from 0.5 to 5000 ppb (Ravenscroft et al., 2009). Severe cases of arsenic contamination through groundwater have been reported worldwide. Long-term revelation with arsenic, a common value for groundwater use, is set to 10 ppb, and it can be set up to 50 ppb. Contamination in groundwater is a worldwide global challenge. Long-term consumption of arsenic-rich groundwater may affect human health, and people may suffer from serious health issues.

II. KINESIS OF AS IN GROUNDWATER

As contamination in groundwater is a severe problem and many natural, and anthropogenic sources ,as depicted in Fig. 1.b. band activities are accountable for this (Das et al .,2020). Metalloid concentration is present in a surplus amount in the groundwater, which is generally attached with the ore deposits. Such contamination in groundwater is the main reason for several health hazards, and contaminated water is the main reason for 80% of diseases (Das and Nag, 2015). Arsenic is associated with ores in the form of sulfidic minerals. These sulfidic minerals are arsenopyrite and pyrite. Groundwater quality deterioration is a result of several geochemical processes (Maliva, 2020). Groundwater exploitation is increasing in many parts of the world due to excessive extraction by pumping and drilling (Barbier, 2019). Under the groundwater, an anaerobic situation exists, which promotes the conditions suitable for arsenopyrite. Arsenopyrite is found abundantly in the environment. Arsenopyrite is found not only in the groundwater but is present abundantly in several rock-forming minerals. These minerals may be oxide, sulfide, carbonate, silicate, phosphate. Arsenic is attached as an ancillary of sulfur and is found in the crystal lattice of various sulfide minerals.

The arsenic cycle in nature occurs due to several natural processes. Accumulation of arsenic in the atmosphere is the result of weathering of rocks and volcanic eruptions due to several tectonic activities inside the earth's surface. Not only this rather a forest fires also contribute to enhancing this proportion in the air. This arsenic in the atmosphere came back to the ground surface through atmospheric precipitation and is sorbed on the organic matter or mix in the groundwater with sediments. Thus arsenic comes in the groundwater and exists in the forms of oxyanions and shows two oxidation states, i.e., arsenite and arsenate (Dembitsky and Levitsky et al., 2004), as shown diagrammatically in Fig. 1. (a). The pH range for the existence of both the form of arsenic is from 6 to 9. In groundwater, arsenic is present as As III or As V (Welch et al., 2000). Thus arsenic contamination in groundwater through natural processes affects our livelihood drastically. Arsenic contamination is the reason for numerous health sicknesses (Mozumder, 2019).

Realgar (As_4S_4) and orpiment (As_2S_3) are the reduced form of arsenic, whereas arsenolite (AS_2O_3) is present in the oxidized state. Arsenic can also be found as sediment having a concentration range of 3 to 10 mg kg^{-1}, based on the type and texture of minerals. The concentration of arsenic is high in the sediments, which are in reduced form and causes severe pollution in groundwater (Polya, 2019). As the depth of sediments increases, the concentration of arsenic also increases. The sediments may also carry oxides of Fe and Al, which play a detrimental role in toxifying the groundwater. The natural processes and many anthropogenic activities are responsible for the contamination of arsenic in the groundwater. These activities include fossil fuel burning, Industrial waste emission, mining, tremendous use of arsenic mixed fungicides, insecticides, and herbicides in the agriculture sector (Shaji et al., 2020). The residue of agricultural pesticides and fertilizers and runoff and industrial waste leach down and form compounds associated with arsenic and make groundwater contaminated, as depicted in Fig. 1. (a).

Among these all activities, coal-burning affects the groundwater reservoirs most. The reflective effect of coal burning is responsible for the contamination in the groundwater environment. Burning causes the emission of arsenic, due to which volatilization of As_4O_6 takes place. As the AS_4O_6

volatilizes, condensation takes place in the flue system, and ultimately, it got mixed with the groundwater system.

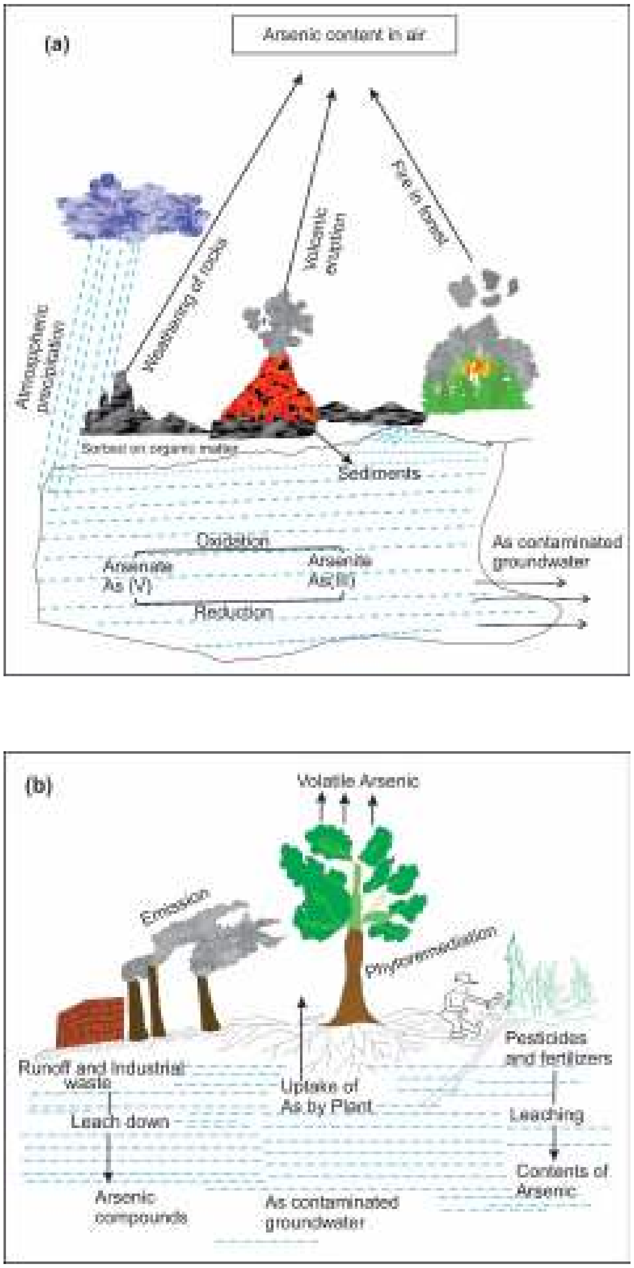

Figure 1. Showing dramatically of arsenic cycle (a.) Natural sources of arsenic cycle; (b.) Anthropogenic sources of arsenic contamination in groundwater.

III. MITIGATION OF GROUNDWATER CONTAMINATED BY AS

Remediation of arsenic-contaminated groundwater comprises scientific as well as socioeconomic measures. The removal of arsenic is a significant issue worldwide due to its hazardous effect. Complete eradication from groundwater is a substantial and complex task that practical approaches can only obtain. These approaches are classified into two categories. These approaches are categorized to show the possible strategies required for the mitigation of arsenic from the groundwater. Mitigation techniques depend on two methods i.e.

1. Use water resources free from arsenic completely.
2. Remove arsenic from water resources altogether.

A. *Use of Arsenic-free Water Sources*

B. *Use of Groundwater at Maximum Depth*

From various lectures and analyses on ground level, it has been reported that the contamination of arsenic occurs mainly in the shallow level of groundwater, whereas the water resources at a depth do not contain toxic arsenic contamination. The aquifers at maximum depth are entirely free from the poisonous effects of arsenic. From research and analysis, it has been found that 5 % of deep tube well waters (more than 150 m depth) has a level of arsenic concentration above 10 ppb, and only 1 % have exceeded this level up to 50 ppb (National Hydrochemical Survey, 2004). It can be concluded that those water resources may be safe and free from As contamination those are operated manually at a maximum depth .eg., tube wells. But the depth may vary location wise. For the delta region in Bengal, the depth of water abstraction is generally considered below 150-200 m deep, while in many other areas, the depth is below 200 m (Union Wise Water Technology Mapping, 2008). While at many places, the concentration of arsenic is less even at shallow depth, i.e., >50 m or > 70 m. But the extraction of groundwater from such a depth is a tedious and expensive process. It requires a high cost for the installation process. The installation process can be possible on a community basis. One of the significant drawbacks is the uncertainty about the available arsenic-free water resources incorporated with groundwater mechanisms (Hoque and Burgess, 2012); saltwater in coastal areas is another cause that creates uncertainty. The high concentration of dissolved heavy metal is one of the significant issues in deteriorating groundwater quality.

C. *Groundwater at the Superficial Level*

The concentration of As at groundwater varies at different levels from region to region and from country to country (Smedley et al., 2002). It has been reported that the plain areas of Ganga and Brahmaputra plains have less contamination of water with arsenic. The range of arsenic contamination is >20% to >50%.In this way, it has been analyzed that in these areas, arsenic-free water can be obtained at a low depth of water. So in such areas bringing water from tube wells at a shallow depth is a good idea and suitable according to the topography (Chakraborti et al., 2010). It has also been reported that among various mitigation techniques, well swapping at a shallow depth to tube wells is the best option. This strategy is found to be beneficial up to 29% (Ahmed et al., 2005). Spatial and temporal variation along the level of arsenic is one of the significant drawbacks of this method. This makes it cumbersome and difficult to predict and makes it unreliable. The concentration of arsenic in tube wells varies from time to time. The concentration of arsenic becomes high in the monsoon season compared to dry winter (Rahman et al., 2014).

D. *Water Resource from Dug Well*

Dug wells are open wells having large diameters. These open wells are another source of getting arsenic-free water (Ahmad et al., 2003). From the various analysis, it has been reported that the level of arsenic was found to be minimum in the open wells. The reason behind this is the dominant oxidative environment and precipitation of Fe (Hira et al., 2007). The National Policy for As Mitigation has been recommended dug wells for safe drinking purposes. But the ongoing study showed that tube wells water is better than open dug water. The reason for the low esteem of dug well water is its intolerable taste and ruthless smell as well as turbidity (Hoque et al., 2004). Another reason for the low popularity of dug well open water is improper handling. Bacterial contamination is one of the most depraved problems in the water of open well dug water. If any person uses such water for drinking purposes without treatment, it may lead to several kinds of disease like typhoid, dysentery, cholera, diarrhoea, and hepatitis. So, for removal of such toxicant chlorination of groundwater is done.

E. *Surface Water*

Arsenic concentration is found to be less in lakes, rivers, and ponds, so these water resources are considered safe for drinking purposes. Arsenic-affected areas lie in the vicinity of a large river, and these large rivers become a suitable mitigation measure for the long run after a decade later. But the same problem of microbial contamination becomes a problem to the ponds and lakes water. Due to this reason, groundwater is preferred over surface water. Surface water can be reintroduced, but it requires proper treatment against microbial contamination. Antimicrobial cures should be managed. The use of pond sand filters and disinfectants can be a good idea to mitigate these problems related to surface water (Yokota et al., 2001). This is the reason why groundwater is preferred over surface water. Consuming surface water for drinking purposes is done after treating with antimicrobial disinfectants and using sand filters for ponds.

F. *Rainwater Use by Harvesting*

Rainwater harvesting is one of the ancient methods for collecting water and for recharging groundwater. Rainwater is used widely for domestic use (WHO., 2011). The use of rainwater is increasing on a wide range for domestic purposes. Safeness and hygiene level determines the feasibility of rainwater for drinking purposes. Rainwater harvesting is suitable in areas having average rainfall up to 1600 mm/year (DPHE., 2008). Harvesting rainwater is an appropriate method for reducing the consumption of arsenic-contaminated water (DPHE National Policy, 2004). Rainwater harvesting is the mere source of drinking water in the coastal areas because of the problem of salinity in the water in shallow as well as deep surface waters (Islam ., 2011). In such places, rainwater harvesting is done in big ponds. Several limitations are incorporated with rainwater harvesting, as installing exceptional surface roofs, and large tanks for storage is expensive (Ahmed, 2003). Another reason is the uneven distribution of rainwater yearly. One of the reasons is microbial contamination which restricts the acceptance of rainwater on a wide range (Islam et al., 2011; Karim et al., 2010). Rainwater is of specific acidic nature and may dissolve some metals and other harmful contaminations along with the storage tank (WHO., 2011; Ahmed., 2005).

IV. MITIGATION STRATEGIES OF GROUNDWATER DECONTAMINATION

Arsenic mitigation techniques depend on various awareness approaches and effective remediation technology. Arsenic removal from groundwater depends basically on the chemistry of the composition of the contaminant in the water. Arsenic is found mainly in the form of As III. Mitigation strategies involve converting As III to As V (Because As III is present in most of the groundwater, after being converted to another form, i.e., As V, the contamination can be reduced from groundwater. This conversion is only due to oxidation. There are various ways by which we can decontaminate the groundwater from the toxicity of arsenic. The techniques of decontamination are discussed as below:

A. Oxidation

Oxidation is necessary to convert the harmful toxic form of arsenic, i.e., As III to As V. The conversion process is perceived by precipitation of As V. As III lies within the neutral pH range (Masscheleyn, 1991). This process of conversion is necessary to obtain pure water for several uses. Arsenate adsorbs better on the solid surface than arsenite (Ghurye and Clifford., 2004; Lupin and Hug ., 2005). For the purpose of oxidation, various oxidants are used. The complete process depends on several reaction kinetics with NH_2Cl, Cl2, H_2O_2, O_3, and ferrate. These all reaction kinetics are of first-order reactions with oxidants and As III. Effective eradication of arsenic from groundwater sources depends upon the concentration of oxidant as well as As III. Conversion of As III to As V in the polluted groundwater through oxidation can be easily done with pure oxygen and air. This conversion is about 54- 57 % (Bajpayi and Chaudhuri., 1999). However, complete oxidation can be obtained by using ozone. An experiment has revealed that when the contamination level in water is low, PEEC-WC nanostructured capsules coated with MnO_2 are more effective than the conventional methods

(Criscuoli et al., 2012). One of the imperative and unpretentious oxidation is solar oxidation. It is used to reduce the harmful content of arsenic in the drinking water in transparent bottles (Mukherjee et al., 2007). Ultraviolet radiation plays a vital role in the presence of other oxidants through the process of catalyzation. Eradication of arsenate and arsenite can be done by adsorbents. The process of conversion from arsenite to arsenate can be achieved after pre-oxidation of arsenite with the help of oxidizing agents. Utilizing oxidizing agents is expensive and causes the generation of toxic by-products, which is not suitable for health (Zhang et al., 2008; Siddiqui and Chaudhry., 2017d). Therefore to escape this trouble, the toxic step of pre-oxidation by using an expensive oxidizing agent must be overcome by solid materials having the characteristic of oxidization (Siddiqui and Chaudhry, 2017d).

One of the novel absorbents is Graphene oxide (GO) which is used to adsorb the pollutant from contaminants and polluted water. Such characteristic is the result of their physiochemical properties (Siddiqui et al., 2019). Biological oxidation plays a vital role in eradicating harmful arsenic from the groundwater. An experiment was conducted, and it was found that *Gallionellaferruginea* and *Leptothrixochracea* are two such microbes that are capable of accelerating iron through biotic oxidation and help to adsorb arsenic (Pallier et al. 2010). Apart from oxidation, a nanofiltration membrane is essential for eradicating arsenic (Song et al., 2015). Arsenic contamination can be reduced by managing aquifer recharge (Newman and Grey, 2019).

B. Coagulation-Flocculation

Formation of flocs by incorporating coagulant is a potential method for removing and eradicating arsenic from groundwater. Cationic coagulants are positively charged and are capable of decreasing the colloidal particles surrounded by a negative charge. This way is essential as it helps aggregate the bigger particles (Choong et al., 2007). The flocculation process results in the formation of particles with more weight. This is only accompanied by the formation of polymeric bridging. In the groundwater, the soluble arsenic gets precipitated upon flocs. These flocs can be easily eradicated from the groundwater. For eradication of arsenic from groundwater Fe and Al centred coagulants are most required (McNeill and M. Edwards., 1995) coagulants among all. By using efficient coagulant like kaolinite and $FeCl_3$ elimination of arsenite and arsenate from groundwater become an easy task (Pallier et al ., 2010).

Aluminium based coagulants like aluminium chloride and the other two are poly aluminium chloride found to be more effective in reducing contamination by using it as a flocculant (Hu et al ., 2012). The efficiency of eradication of arsenite and arsenate improves after using Aluminium species. When the efficiency of both the coagulant was compared, it was found that among both coagulants, Fe was better than aluminium (Ravenscroft et al., 2009). Therefore it was found that coagulation and flocculation is an effective process of removing arsenic from groundwater. By adopting these methods, arsenic contamination can be mitigated easily from the aquifer resources.

C. Adsorption

Decontamination of groundwater can be done by using this physicochemical process. It is an efficient technique to purify the pollutant from groundwater. In this mitigation technique, solid or liquid surfaces are used to retain the contaminant. These contaminants may be gases or liquid pollutants (Sarkar and Paul., 2016). The process of adsorption has proved to be more efficient in eradicating arsenic on the activated surface from groundwater. This technique is gaining popularity nowadays because of its property of sludge-free operation. This technique incorporates various adsorbents, which are reusable (Mohan and Pittman ., 2007). Some adsorbents are restricted to laboratory use like biochar, activated alumina, and ferric hydroxide granulated form (Singh et al., 2018). Remediation of groundwater from toxic arsenic through adsorption depends upon the pH. The degree of adsorption is influenced by ions like carbonate, silicate, $Ca_{2+,}$ and phosphate (Lin and Wu., 2001). Adsorption of As III and As V from groundwater is done with the help of ferric hydroxide and hydrous ferric oxide (Giles et al .,2011). One of the significant problems that occur with adsorption is the high concentration of iron in the groundwater. In this way, it creates a clog in the filter material, consequently reduces the lifespan of the filter (Bamwsp et al., 2001). That is why the adsorption filter should be maintained properly to keep away the problem of coagulation. The dissolution of arsenic has taken an essential step in various regions of the world. Different modern and conventional techniques are used for the eradication of arsenic, along with some hybrid skills.

In Vietnam, a very cheap and effective adsorbent, laterite, is used, which is not so expensive and can be used in a sustainable filtration system (Nguyen et al., 2020). India is rich in clay laterite; therefore, it can be used in the mitigation of arsenic-contaminated water (Shaji et al., 2020).

D. Ion-Exchange

The exchange of ions between an electrolyte and within electrolyte and solution is known as ion exchange. Ion exchange is the process that leads to purification. It is widely used to separate the pollutant and be efficient in decontaminating the aqueous contaminant from groundwater. These contaminants are removed with the help of compact and polymeric ion exchangers (Ghosh et al., 2019).

Ion exchangers may be cationic and anionic. Cation exchangers are used to exchanging the positive ions, and anion exchangers are used to trading the negative ions. Apart from the cationic and anionic exchangers, some exchangers can exchange cations as well as anions. These are known as amphoteric exchangers. Size, charge, and structure of the ions are the key characteristics used to determine the potential of the ion-exchangers. Synthetic resin beds are used as a platform to carry out the process of ion-exchangers. Water contaminated with arsenic is passed through the artificial resin bed, which is in solid form is able to exchange the contaminated arsenic water in the liquid phase. Decontamination of arsenic from groundwater can be done efficiently with the help of ion exchangers. These ion exchangers may be clay, soil humus, zeolites and montmorillonite. Cation exchangers and anion exchangers are ion exchangers that can exchange positive and negative ions, respectively. However, amphoteric exchangers are those which can exchange anions as well as cations. The simultaneous exchange of cations, as well as anions, is more effective in the mitigation of harmful toxicant heavy metals from the aqueous resources. There are various factors upon which the potential of ion exchangers depends. These factors are the size of ions, chemical structure of ions, and pH of the aqueous solution. Generally, synthetic resin beds are selected for the ion exchange process. Resin beds play an essential role in the extraction of arsenic ions from the groundwater. When water contaminated with toxic arsenic passes through the solid resin beds, an exchange process occurs between the ions of the liquid phase and the solid phase. Consequently, the ions of arsenic get absorbed in the resin bed. Exchange of contaminated liquid ions occurs with the equivalent numbers of stable ions present in the solid bed. Lanthanum (La III), iron (Fe III), copper (Cu II), and Cerium (Ce IV) are placed in the category of positive ion exchangers or cationic exchangers. At the same time, amber lite XAD-7 carrying TiO_2 is known as anionic exchangers (Mohan and Pittman, 2007; Sarkar and Paul, 2016).On the other side, some ions like $SO_4{}^{2-}$, $CO_3{}^{2-}$, HCO_3 hamper the process of arsenic removal. The reason behind this hindrance is an affinity towards resins.

E. Membrane Process

Membrane filtration is a way to mitigate harmful contaminant particles. In this process of separation, the specific ion is eradicated. In this process, a particular ion can be simply detached. It is a very reliable method. The membrane is made up of to certain kind of tissue which is used for filtering arsenic consist several holes. This allows for the passage of selective ions, whereas other ions are restricted to pass within this membrane.

The behaviors in which these barriers are designed are unique. Pressure difference or potential difference act as a driving force during the entire process. Such a membrane process is categorized in two broad different methods.

- Reverse osmosis
- Filtration by low-pressure membrane

Reverse osmosis and Nano filtration come under a high-pressure membrane, whereas ultrafiltration is the process that comes under a low-pressure membrane. The eradication process in which a high-pressure membrane is used is based on the principle of chemical diffusion, while physical sieving is the base of the low-pressure membrane (Shih 2005).

1) Reverse Osmosis

Reverse osmosis is one of the well-known and influential choices used for the eradication of arsenic from groundwater. The membrane used in this method is based on the low diffusivity of water while the pressure remains high. By this process, we can eradicate As (V) up to 90 percent by using a cellulose–acetate membrane. At the same time, the removal efficiency of As (III) is less i.e., up to 70 percent. In the process of reverse osmosis, shortened membrane life is used for the oxidation of As (III) to As (V), which is not possible (Shih, 2005; Ning, 2002; Clifford et al., 1986; Fox, 1989).

2) Filtration by Low-Pressure Membrane

This is a kind of microfiltration process in which the membrane used is of low pressure. The pore size is large to extract and eradicate the dissolved arsenic species with a colloidal nature. The removal is done efficiently from the water (Shih, 2005). This method only eliminates arsenic matter. This removal process is rare, and usually, the process of coagulation and flocculation is smashed with it to enhance the molecular weight of these particles (Ghurye and Clifford, 2004). The eradication efficiency of arsenic particles can be increased using an adsorbent of ferric chloride or ferric sulfate. Any cationic flocculants can be used for this (Han et al., 2002). Ferric chloride and ferric sulfate are iron-based coagulants capable of making iron oxyhydroxide after getting hydrolyze with water and, as a result, make a net positive charge on the surface outside (Pal et al., 2001). Arsenite species exist with the pH range 4 to 10, whereas this pH range results in negative for the arsenate species. Therefore it may be endorsed that the eradication of arsenate is faster. This fortification became possible due to the surface complexation (Meng et al., 2000). Another technique known as ultrafiltration is a physical sieving method based on low-pressure practice. Several bench experiments have shown that the neutrally charged species are less effective. The efficiency increases with the negativity.

V. GROUNDWATER CONTAMINANT REMOVAL BY NATURAL REMEDIATORS

The flowchart depicted in Fig. (2) represent the removal of groundwater contaminant with bio-organism like prokaryotes, eukaryotes and aquatic macrophytes **.**

A. Eradicating Arsenic Using Bio-organism

1) Prokaryotes

Arsenic contamination can be eradicated efficiently by using bio-organisms in groundwater. In other words, we can say that bio-organisms act like powerful bio-weapon to reduce the contamination of arsenic from aqueous water resources (Taggart and Starr ,2009; Singh et al., 2020). The body of prokaryotes has been designed in an effective way to counteract the harmful effects of arsenic contamination. The prokaryotes have been designed internally to eradicate the toxic heavy metal As from groundwater. Prokaryotes have particular approaches for detoxification.

a. Dynamic arsenic extrusion
b. Transforming arsenic in organic forms
c. Intracellular chelation

Many techniques for As remediation has proved to be inefficient because As acts as an electron donor or acceptor donor in the extreme toxicity of contamination and acts like an active component in some bacteria (Tsai et al., 2009).Glycerol and phosphate transporter are used to occupied the arsenite and arsenate because both of them have similar structures. *Pseudomonas putida* and *Leishmania major* (Gourbal et al., 2004) are proficient in the transference of As(III) through the cell membrane (Tsai et al., 2009; Rahman et al., 2014).In anaerobic conditions, *Sulfurospirillum* and *Geobacter* species play an important role in the conversion of arsenate to arsenite (Héry et al., 2008). Based on the techniques of 16S r RNA gene and the result of analysis of phylogenesis, it was concluded that Sulfurospirillum and Geobacter species have a possibility to be involved in arsenate respiration in anaerobic environments to transform As(V) to As(III).

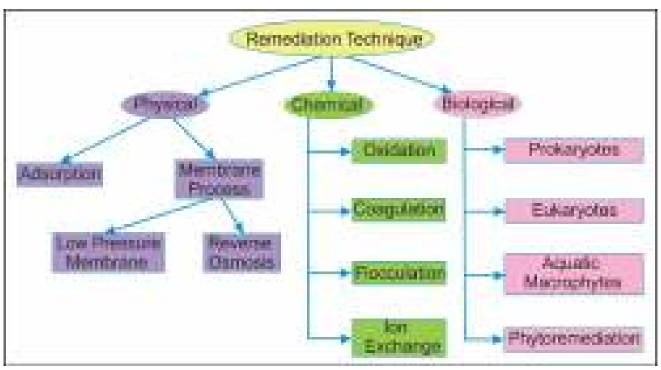

Figure 2. Physical Chemical and Biological Remediation technique of arsenic removal from groundwater.

2) Eukaryotes

Eukaryotes are the organism with a definite nucleus with a membrane-enclosed organelle. Arsenic enters the plant body by using phosphate transporters. The decontamination process starts instantly as the arsenic is imposed in the plant body and reduces the effects of cytotoxicity in arsenic. ARR1, ARR2, ARR3 are genes in yeast that induce tolerance capability for arsenic (Rahman et al., 2014). Silicon transporter is the pathway of uptake in rice plants. Several genes are modified through genetic engineering, which is responsible for the incursion of arsenic. In the case of leguminous plants in arsenic stressed conditions, holo PCs (hPCs) along with the other compounds produced and play an essential role in detoxifying the arsenic contamination (Grill et al. 2007). A study revealed that proficient sporophytes of Pteris vittata could store As (III) inside the leaves (Pickering et al., 2006), whereas another study concluded that *Pteris vittata* could store arsenic in their roots (Duan et al. 2005). Cereal plants like maize have also been found to be proficient in the storage of toxic contaminants of arsenic from the soil. Other plants parts like bracts stems, leaves, and kernels are also used for the storage of arsenic (Ding et al. 2011 and Liu et al.,2012).

3) Aquatic macrophytes

Not only the prokaryotes and eukaryotes but also aquatic macrophytes play an important role in decontaminating toxic heavy metal arsenic from the water resources (Bergqvist and Greger, 2012). Different species of aquatic macrophytes are present, which can hyper-accumulate arsenic from groundwater (Rubio et al., 2010). Algal species are also known to decontaminate arsenic from water resources (Ghosh et al., 2019). Some arsenic accumulators are *Portulaca tuberose*, *Eclipta alba, Lemna gibba*, *Limnanthes spp,* and *Portulaca oleracea*. *Hydrilla verticillata* is known widely for eradicating arsenic from aqua sources (Srivastava et al., 2011). Aquatic plants such as *Cyperus difformis*, *Eichornia crassipes* and fern species *Marsilea* is used to decontaminate arsenic contamination from water. Lemna gibba L plants of Lemnaceae family can eradicate the arsenic contamination from groundwater resources (Mkandawire and Dudel 2007). Many studies on aquatic macrophytes have concluded that these plants are efficient in eradication arsenic contamination from groundwater Mishra et al., 2008; Tripathi et al., 2008; Zhang et al., 2008).

VI. MITIGATION OF ARSENIC BY PHYTOREMEDIATION TECHNIQUE

Phytoremediation is a green technique in which green plants are used to decontaminate harmful toxicants from the environment. Phytoremediation is based on natural plants remediation system. It remediates the harmful toxic contaminants from groundwater, soil and surface. Therefore it is a unique plant based and appealingly attractive approach. The aim of this novel technique is to mineralize the organic pollutants in to non-hazardous form. Phytoremediation uses discerning plants to decontaminate environmental pollution. The plants which are used for remediating treacherous devastating contaminant must be of rapid growth physiology, having high biomass, fibrous root structure. Cultivation technique must be easy and harvesting should be tranquil. Phytoremediating plants must have tolerable to heavy, toxic and hazardous metals and have the feature of easily operate (Patra et al, 2019).These plants maintain the ecological stability and restore conservational vigor. It comprises several techniques, e.g., Phytoextraction, Phytostabilization phytofiltration, phytovolatilization, photodegradation, phytodegradation. These techniques have their own mechanism, which plays an important role in mitigating environmental pollution by either extracting heavy metals in roots, stems, leaves from soil or stabilizing them in the soil so that they can’t mobilize within the plant system.

A. Phytoextraction

Phytoextraction is also known as phytosequestration or phytoaccumulation is a technique of mitigating toxic contaminant from soil by using green hyperaccumulators. The roots of these plants are engage in uptake of noxious substances. This hazardous toxic contaminant is stored in harvestable plant parts.

Before understanding the mechanism it is important to understand the basic key element of any toxic contaminant. The easiness and intricacy of remediating any contaminant depends upon the behavior and type of pollutant. Toxic heavy metals are present as ions as well as complex organometallic complexes. The solubility of these toxic contaminant also affected by several environmental factors like pH, cation and anion exchange capacity and solubility of metals. The solubility or extraction of metals from soil is through by roots. These harmful heavy metal contaminant is captured by the root cell. The extraction of contaminant through roots of plant basically entails three steps.

1. The metal present in the soil should dissolve readily so that the roots can absorb them easily.
2. The plants roots should be capable to absorb the soluble metals immediately.
3. The chelating efficiency of plants must be high to chelate the metals to protect it and to make the metals more mobile. The chelated metal must be stored in plants parts.

Any organic acid or phytochelatins are the chelating agents and act as very important key for the process of phytoextraction. Among the techniques of phytoremediation, phytoextraction is one of the most challenging and perplexing process and reason lies within its capacity of extracting high amount of metals present in the soil.

Further phytoextraction is divided in two kinds, one is induced or chelate assisted phytoextraction and another is continuous or long term phytoextraction. Among these two, chelate assisted phytoextraction is more reliable and use widely on a commercial basis.

1) Hyper accumulators: Role in Phytoremediation

Hyper accumulators plants are the most preferred ones for Phytoextraction.These techniques of phytoremediation efficiently volatilize environmental contaminants from above-ground parts (stem, leaves, and seed) and below-ground parts (roots) of plants, as shown in Fig. 1. (b). Plants which are used for the remediation of environmental pollution are categorized in to three groups. These are a.) Excluders b.) Accumulators and c.) Indicators.

Excluders are those which play an important role in preventing the process of leaching of hazardous, toxic heavy metals become stable and thus keep the marginal water reservoirs clean and safe (Lasat, 2002).The excluders also checks the way of entry of harmful metals in the root cells of plants (de Vos et al., 1991).While accumulators have mechanism in which the biomass of the plants are used for the accretion of heavy metals. They do not allow for the movement of heavy metals in the roots. Apart from these two, indicators are those plants which have the capacity of reflection of toxic precarious metals. (Mc Grath et al., 1997). Hence there is no deny to say that hyper–accumulators plants are precious gift of nature but human beings do not use them efficiently and some of them being exploited for the techniques of phytoremediaion. So we should use them efficiently with a goal of having sustainable environmental pollution remediation. Hyper accumulators are plants with special intrinsic property. These plants have capacity to accumulate the heavy metals at a range of 50 to 500 times. Whereas the normal plants do not have the capacity to uptake heavy metals in this range (Lasat et al., 2000). Hyper accumulating plants can also accumulate heavy metals in their roots as well as shoots without showing any noxious indications on plants. Bioconcentration factor and translocation factor are used for measuring the efficacy of hyperaccumulators plants. The value of Bioconcentration factor is more than 1, sometimes it may be 50-100.The percentage of angiosperm to fell in the category of hyper accumulators is very low. It is estimated as lower than 0.2% (Baker and Whiting, 2002; Rascio and Navarie-Izzo, 2011). Hyperaccumulator plants have mechanism to remove the heavy metals from soil. These plants depend upon factors like soil pH, micro fauna, moisture efficiency and type of heavy metals present in the soil. Critical interaction relies between the rhizosphere of hyper-accumulators, soil ,microbes and toxic contaminant of heavy metals .In this way the removal of contaminant become more proficient (Sarwar et al., 2017). Hyperaccumulators plants belong to many angiospermic families. Some of them are Euphorbiaceae, Poaceae, Cyperaceae, Fabaceae Brassicaceae, Lamiaceae Asteraceae and Caryophyllaceous (Padmavathiamma and Li, 2007).

B. Rhizodegradation

Rhizodegradation is also known as phytostimulation. As the name indicates, it is the enhancement of activity of soil rhizospheric microorganisms for degradation of harmful and toxic contaminant. This process occurs in the rhizospheric zone of soil. These beneficial microorganisms are stimulated by the carbohydrates and acids secreted from the roots of plants and as a result they break down the harmful organic contaminant in to the non-toxic forms. This technique is useful in degrading the harmful compounds like petroleum hydrocarbons, PCBs and PAHs. Not only the terrestrial plants but aquatic plants also play an important role in degradation of contaminants.

C. Phytostabilization

Phytostabilization is the process of remediation of contaminant from polluted soil. It reduces the movement of substance in the soil by restraining the leaching of materials. The plants restrict the mobilization of contaminants and bind them with the soil particles and thus these became less available for the further use. In this way the plants are capable to evacuate a substance which has the property of produce a chemical response and as a result of which alters the toxic and heavy metal contaminant in a non-toxic system. Stabilization of these harmful contaminants degrade the bioavailability of toxic contaminant by reducing the erosion, leaching as well as run-off.

Basically the phytostabilization technique comes in to light when the mitigation of environmental pollution by using green plants was not on the top priority list. At that time mitigation process was done with the help of some amendments which was used to fix or immobilize these harmful contaminants in the soil (Berti and Cunningham, 2000). Phytostabilization is also known as phytorestoration. This technique immobilizes or fixes the harmful contaminant in soil by the formation of a vegetative cap in the rhizosphere. The vegetative cap in the rhizosphere is accompanied by the mechanism of sequestration. The sequestration of contaminant comprises binding and sorption of pollutant as a result of which this harmful and toxic contaminant is not available for human, wildlife and livestock feed routine (Munshower, 1994; Cunningham et al., 1995; Wong, 2003).

Phytostabilization do not deal with the complete eradication of heavy metal from the contaminant site rather it arrange with the complete stabilization of them in to the soil and thus mitigate the risk of being transferred to the food chain and feed habits of livestock. To add some more effects in phytostabilization phosphatic fertilizers, organic matters, iron oxyhydroxide and manganese oxyhydroxide and clay minerals play an important role. These natural or synthetic components either fix the contaminant in the soil or make some chemical alterations in the soil as a result of which these contaminant are unable to move from soil to the plant parts. The plants which are used for phytostabilization must be easy to grow with vigorous canopies and root system and must be tolerant to toxic heavy metals. Phytostabilization has many advantages over other phytoremediation techniques like its easiness to implement, less expensive and mainly in this process harmful heavy metals do not move inside the plants (Cunningham and Berti, 2000).

D. Phytodegradation

This remediation technique is specifically for the degradation of organic pollutant in the soil or within the plant body with the help of microorganism. Phytodegradation or phytotransformation process is very attractive and presents a beautiful phenomenon regarding the degradation of contaminants. The process stimulates with the secretion of some enzymes through the plant roots. The enzymes are used for the breakdown of organic compounds and the broken molecules of these compounds are lost through transpiration by plant system. These organic compound may be herbicides, trichloroethylene and methyl tert-butyl ether.

E. Rhizofiltration

Rhizofiltration or phytofiltration is the remediation technique to purify the groundwater or any other water sources by the help of terrestrial or aquatic plants. In this process a mass of roots are used to filter and remove toxic and harmful contaminant from water. The contaminant get absorbed in or adsorbed to the roots. Through this process remediation of lead (Pb), cadmium (Cd), copper (Cu), nickel (Ni), zinc (Zn) and chromium (Cr) are done. Retention of these contaminant are mostly within the roots. (Chaudhry et al., 1998). Studies shows that plants like sunflower, tobacco, musturd, spinach, rye, Indian mustard and maize have potential to remove lead from the effluent.

F. Phytovolatilization

Phytovolatilization is the process of removal of organic and inorganic pollutants in the atmosphere by converting them in the volatile gases. This organic contaminant came in to plant system through the polluted water. These volatile gases which are volatilized in to atmosphere are of very low concentration and thus do not harm the atmosphere.

Phytovolatilization plays an important role in remediation of mercury. In the whole process Hg^{+2} get converted in to less toxic HgO and volatilized in to the atmosphere. This way of mitigating environmental contaminant is valuable because it is free from any disposal of hazardous, toxic and heavy metal contaminant. It includes no disturbance to the sites. According to a report published, this technique was found more controversial among all the other techniques of phytoremediation because it has been said that the mercury which was volatilized in to the atmosphere, recycled and through precipitation again deposit in the ecosystem (Henry, 2000).

G. Phytoremediation Efficiency of Aquatic plant species for removal of arsenic- contamination in water.

Aquatic plant species either macrophytes or microphytes are very effective for removal of high arsenic contamination in water. To understand the mechanism and clarity regarding the phytoremediating appliance, three aquatic water-bodies were used. These water bodies were water-hyacinth, Cladophora and Chlorodesmis spp. These aquatic species effectively remove the toxic arsenic contamination from water bodies. So, for this purpose, water hyacinth were collected from water system .These aquatic species should be collected in a way that its fibrous roots system must be remain safe because they play an important role in the phytoremediation process in absorbing the metal concentration in through roots.

1) Phytofiltration efficiency of aquatic plant Micranthemum umbrosum

An ornamental aquatic plant *Micranthemum umbrosum* is capable of filter the hazardous harmful toxic contaminant in the form of heavy metals. They have long roots and by the help of mass of roots they are capable to eliminate the detrimental contaminant or nutrients. The pollutant or contaminant are absorbed or may become adsorbed on the roots. These plants are proficient to clean the groundwater when planted and can also remove the pollutants in the waste water or contaminated water in the off site location.

A study was conducted to understand the mechanism of phytofiltration technique of the aquatic ornamental plant *Micranthemum umbrosum*. In this study phytofiltration technique for the heavy metal arsenic and cadmium was evaluated. The experiment was designed in a better way and the aquatic plant *Micranthemum umbrosum* was cultured in a hydroponic culture for seven days. Heavy metals Cd and As were observed in leaves and water. Sample analysis was done with plant and water samples. After analysis the pattern of uptake was found. The highest concentration was obtained in roots. As compare to roots the concentration was less in stems and the least concentration was observed in the leaves. Arsenic and Cadmium concentration in the solution was observed for each day. In the total duration of seven days during the experiment it was observed that the concentration of arsenic and cadmium decreases significantly up to 5th and 4th day respectively. As the seven days completed it was found that the arsenic and cadmium concentration remaining in the solution was less than 50 u/L & 100 ml u/g. After observing the pattern of heavy metal accumulation it was found that the concentration level of this harmful toxicant was found more in roots as compared to stems and roots. There are various plants in nature which play a major role in the removal of arsenic from soil and groundwater. Water hyacinth, lesser duck weed, water lettuce, butterfly fern and several others as listed in Table 1 are important in the exclusion of arsenic.

VII. GROUNDWATER FOR SUSTAINABLE DEVELOPMENT

Groundwater contamination is a significant issue in the current days as it affects the health of all living organisms and deteriorates the environmental quality. This contamination is due to wastewater disposal in water resources, leaching of contaminated water, or excessive fertilizers and pesticides effect (Jia et al., 2020; Wang et al., 2019; Zhang et al., 2020). Sustainably using groundwater is the most vital thing for human life. Sustainable use of groundwater is necessary for life. Groundwater is present abundantly on earth. Groundwater is the essential source for maintaining and balancing the ecosystem. The ecosystem is supported by obtaining water from groundwater. Not only the water but several minerals and nutrients are also provided for the ecosystem. A large population on earth depends upon groundwater for the production of food for nourishment and vitality. About 100 million hectares of arable lands depend upon groundwater for irrigation purposes, and above 40% of the water from groundwater is used essentially. Human development is directly or indirectly related to groundwater. Groundwater also play an essential role in poverty eradication. Groundwater moves at a slow speed. Under natural conditions rate of moving groundwater is 0.01 and 10 m per day. The impact of climatic fluctuations and pollution can be overcome from groundwater with the help of geological

Table I: List of plants useful in removal of Arsenic in water

Sl.No.	Botanic-al Name	Common name	Reference
1.	*Eichhornia crassipes*	Water hyacinth	Alvarado et al., 2008, Mishra and Tripathi 2009., Saleh 2012
2.	*Lemma minor*	Lesser duck weed	Zayed et al., 1998
3.	*Pteris vittata*	Chnese brake fern	Sakakibara et al., 2010
4.	*Pistia stratiotes*	Water lettuce	Akter et al., 2014; Das et al., 2014; Farnese et al., 2014
5.	*Lemna*	Duckweeds	Khellaf and Zerdaoui (2009)
6.	*Salvinia minima, Salvinia molesta and Salvinia natans*	Butterfly fern	Klopper., 2011
7.	*Azolla pinnata*	fern	Klopper., 2011
8.	*Lepidium sativum L.*	Garden cress	Gunduz et al., 2012; Smolinska and Szczodrowska 2016
9.	*Arundo donax*	Giant cane	Guarino et al., 2020
10.	*Phragnites australis*	Common reed	Rodriguez and Alarcon .,2019
11.	*Vetivaria zizinoids*	Vetiver grass	Taleei ,2018
12.	*Typha latifolia*	Broadleaf cattail	Adriana ., 2013
13.	*Hydrilla verticillata*	Water thyme	Zhao et al., 2019
14.	*Ceratophyllum demersum*	Hornwort	Khang et al., 2012
15.	*Myriophyllum spicatum*	Parrot feather	Abu bakar et al., 2013

formations. Therefore we can say that in every aspect of life, whether it is human beings or irrigation purpose or development of country economically, the demand for groundwater is indispensable (Qi et al., 2020) Our primary duty is to use groundwater efficiently so that we can reach the goals of sustainable development.

CONCLUSION

Groundwater is one of the most essential and indispensable resources which supports human beings to lead their daily life, not only for drinking purposes but also for several domestic, agricultural and industrial purposes. Due to the increase in population and demand, there is an urgent need to keep groundwater resources free from hazardous heavy metal contaminants and to use them sustainably. At first, it is essential to understand the sources and kinesis of arsenic in water. The worldwide overview of arsenic in water is a severe ecological view, and it is also necessary to understand the contamination of arsenic in groundwater. Mitigation of groundwater contaminated by arsenic can be corrected by using deep groundwater, shallow groundwater, i.e., well switching, dug well water, surface water, and rainwater harvesting. These physical methods are found effective for the decontamination of a toxicant from the groundwater. Chemical removal depends upon some techniques like ion exchange, coagulation-flocculation, oxidation, membrane process, low-pressure membrane filtration, etc. Not only these physical and chemical mitigation methods, but some natural technics are also available. Mitigation of arsenic by phytoremediation technique is widely used nowadays. Phytoremediation is the best and very effective green technique that is used to remove arsenic from groundwater with the help of natural trees. Groundwater quality analysis is a crucial parameter that is directly related to human growth and development. Groundwater use for sustainable development is an essential step as it is necessary to save it for future generations also.

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