

# LOW COST INDIGENOUS TECHNOLOGIES FOR REMOVAL OF ARSENIC FROM DRINKING WATER: CASE STUDY OF PAKISTAN

Zulfiqar Ali Bhatti<sup>1,\*</sup>, Khadija Qureshi<sup>1</sup>, Muhammad Yar Khuhawar<sup>2</sup>, Abdul Waheed Bhutto<sup>3</sup>, Zulfiqar Ali Solangi<sup>1</sup>, Imran Nazir Unar<sup>1</sup>

<sup>1</sup>Department of Chemical Engineering, Mehran University of Engineering and Technology, Jamshoro, Sindh, Pakistan

<sup>2</sup>Institute of Advanced Research Studies in Chemical Sciences, University of Sindh, Jamshoro, Sindh, Pakistan

<sup>3</sup>Department of Chemical Engineering, Dawood University of Engineering & Technology, Karachi, Pakistan

## ABSTRACT

Arsenic (As) is among one of the most toxic naturally occurring metallic elements. Its occurrence in water resources causes severe health hazards. The viable solution to address this health hazard, is to treat As contaminated water. This study presents an overview of naturally occurring As in water resources and various As removal techniques adapted to treat As contaminated water. The study specifically focuses on low cost indigenous technologies which can be easily adopted to treat As from drinking water resources, especially in remote areas. The review reports that various low cost materials have been scrutinized for As removal from water, however, challenges such as a simpler process for development at local levels are still prevailing. These challenges have to be resolved in order to offer competent As removal technologies for underdeveloped regions of developing countries.

**Key Words:** *Arsenic treatment methods, drinking water, adsorption method, arsenic removal, low cost adsorbents.*

## 1. INTRODUCTION

Arsenic (As) is present naturally in earth, mixing with water by leaching from mineral deposits and soil causing health issues in different locations of the globe [1]. Elevated As concentrations have been discovered in potable water resources globally and it intimidates to more than 200 million individuals in both developing and developed countries [2]. The global abundance of As is about 1.50 to 3.0 mg/ kg [3]. As is a poisonous metalloid which is mainly available in inorganic forms as arsenite As (III) and arsenate As (V), in water [4]. Arsenite is comparatively more hazardous than arsenate, because As(III) attaches to single but with higher attraction to sulfhydryl groups that chemically reacts with various types of proteins and restrain their activity [5].

As affects the human body by many ways such as contaminated food, vegetables, fruits, milk but the main source is the water [6]. The presence of As in water causes a number of diseases such as, cancer, cardiovascular diseases, skin cancer, diabetes and black foot disease [7]. Hence treatment of As contaminated water and provision of safe potable water to the society is an imperative concern at present.

After the conduct of successful field tests in different countries, a number of community-based and small-scale methodologies for As treatment were implemented based on batch processes and column operations [8]. The scientists have studied various As removal technologies and they found adsorption method effective in reducing the As concentration in treated water. The researchers have tested different adsorbents for instance activated carbon, metal oxides, organic polymers, silica and waste biomass sorbents [9]. The research shows that the iron and aluminium hydroxides and oxides are comparatively more effective amongst metal oxide adsorbents [10]. Nevertheless applicability of these conventional and non-conventional methodologies is restrained due to deficiency to regenerate and reuse the adsorbents [11]. The goal of present study is to present a comprehensive survey of efforts regarding remediation techniques of As adopted by Asian countries.

## 2. ARSENIC IN DRINKING WATER

World Health Organization (WHO) and US Environmental Protection Agency has suggested the safe values of As in potable water as 10 ppb in order to reduce health risk [3]. Large population of world is in danger of As toxicity through As contaminated ground water and it is one of the big environmental challenge for mankind [12]. The occurrence of As in underground water is because of the geological activities of rock sand soils which releases minerals with the passage of time. As the water is taken out by boring and tube wells it might contain traceable concentrations of this toxic element. The groundwater arsenic research community was producing vast assets during the last three decades. The USA appears as the leading country in total number of publications followed by a group of Asian countries (India,

China, Bangladesh, Japan, and Taiwan) which are very concerned about the As problem [13]. As contaminated groundwater is showing health risks to more than 10 million people in Southeast Asia, where ground water is used as potable water pertains the major cause of inorganic As. In the USA, boring water is a major supply of As, whose concentration varies widely and regionally [14]. Drinking water contamination by As is also widespread throughout China [15]. The four major incidents of As toxicity reported from Asian continent in terms of severity of presence are Bangladesh, Indian state of West Bengal, Mongolia and Taiwan. Each year Asian countries report new As groundwater contamination incidents [16].

### 3. ARSENIC CONTAMINATION IN PAKISTAN

High As concentrations in river and ground water were mentioned in several areas of Pakistan e.g. Jamshoro district [4], Matiari [17] and Khairpur [18], Manchar lake [19], Tharparkar [20], Muzaffargarh [21], Kohistan[22]. As concentrations in Pakistan reported in literature are summarized in Table 1. In Pakistan, water from various sources is polluted with As particularly in Sindh and Punjab provinces. 16% to 36% people of Sindh Province are in contact to 10 ppb and 50 ppb of As respectively. As range is 3 to 50 ppb or  $\mu\text{g/L}$  and 13 to 106 ppb in surface and boring water of Jamshoro district respectively [4]. On the left bank of river Indus Khairpur and Matiari districts 37% of the samples were in the range of  $50 \geq 50$  ppb As while 15% samples were found to have elevated amounts of 250 ppb As [18]. 23% of wells in the district Khairpur were found affected with As contamination and the overall presence of As skin lesions was found to be 13.5% in the study involving a survey of more than 3,000 individuals [18].

Table 1. Arsenic concentration in various sources of drinking water in Pakistan

Location in Pakistan	Source of As	Concentration of As	Reference
Jamshoro district, Sindh	Surface water Underground water	3-50 $\mu\text{g/L}$ 13-106 $\mu\text{g/L}$	[4]
Different regions of Sindh	Lake, Canal and river water	$90 \pm 9.20$ $\mu\text{g/L}$ $20 \pm 9.60$ $\mu\text{g/L}$ $15.6 \pm 7.90$ $\mu\text{g/L}$	[23]
Matiari and Khairpur districts, Sindh	Ground water	50-250 $\mu\text{g/L}$	[24]
Manchar lake, Sindh	Lake water	35-157 $\mu\text{g/L}$	[19]
Neighboring areas of Manchar lake, Sindh	Ground water	23.3-96.3 $\mu\text{g/L}$	[19]
Nagarparkar, subdistrict of Tharparkar, Sindh	Surface water and Agricultural soil	360-683 $\mu\text{g/L}$ and 110-266 mg/kg	[25]
Muzaffargarh District of Punjab	Ground water in urban areas	>50 $\mu\text{g/L}$	[21]
Jijal-Dubair of Kohistan region	Surface and ground water	<0.03-0.5 ppb & 0.13-16.7 ppb	[22]
Besham of Kohistan region	Surface and ground water	0.05-1.11 $\mu\text{g/L}$ , <0.03-0.45 $\mu\text{g/L}$	[22]
Alpuri of Kohistan region	Surface and ground water	0.98-2.02 ppb and <0.03-0.02 ppb	[22]
Dera Ghazi Khan	Ground water	1- 29 $\mu\text{g/L}$	[26]
Faiz Ganj, Khairpur	Canal and Tube well water	$5.44 \pm 0.07$ $\mu\text{g/L}$ and $15.4 \pm 2.31$ $\mu\text{g/L}$	[27]
Thari Mirwah, Khairpur	Canal and Tube well water	$7.00 \pm 0.09$ $\mu\text{g/L}$ and $31.0 \pm 8.21$ $\mu\text{g/L}$	[27]
Gambat, Khairpur	Canal and Tube well water	$8.20 \pm 0.12$ $\mu\text{g/L}$ and $98.5 \pm 68.7$ $\mu\text{g/L}$	[27]
Faiz Ganj, Khairpur	Agricultural land irrigated with Canal and Tube well water	$4.26 \pm 8.21$ $\mu\text{g/L}$ and $6.10 \pm 3.10$ $\mu\text{g/L}$	[27]
Thari Mirwah, Khairpur	Agricultural land irrigated with Canal and Tube well water	$4.94 \pm 6.25$ $\mu\text{g/L}$ and $29.5 \pm 12.6$ $\mu\text{g/L}$	[27]

Gambat, Khairpur	Agricultural land irrigated with Canal and Tube well water	5.28 ± 10.6 µg/L and 57.3 ± 18.8 µg/L	[27]
Lahore and Kasur districts, Punjab	Ground water Rain water	32-1900 mg/L 10-90 µg/L	[28]
Haripur Basin	Surface water Ground water	0.6-5.48 µg/L <0.15-3.72 µg/L	[29]
River Ravi	Surface water	98 ± 50 µg/L	[30]
Kalalanwala village, Punjab	Ground water Surface soil	2.4 mg/L 10.2 mg/kg	[31]
Hyderabad	Ground water	4.5-10.7 µg/L	[32]
Thari Mirwah, Khairpur	Ground water	14.5-47.7 µg/L	
Gambat, Khairpur	Ground water	38.8-362 µg/L	
Thar desert	Stored rain water	194-683 µg/L	[25]

The study [19] presented the As results in the samples of sediment and water of Manchar lake Sindh, Pakistan and the adjacent agricultural lands during 2005-2007. It was revealed that As levels in farming land and lake sediment vary between 9 to 46 and 11 to 56 mg/kg, respectively. The concentration of As in ground and leafy vegetables were also compared. Ground veggies (0.05–0.25 mg/kg) and grain crops (0.25–0.37 mg/kg) showed lower As levels than leafy vegetables (0.90–1.20 mg/kg). The average As intake for adults from foodstuffs of agricultural lands watered with lake water was measured 343.5 µg/day.

As concentrations were analysed in Nagarparkar, subdistrict of Tharparkar, Sindh, Pakistan during 2010-2012 and reported in 2014 [20]. As levels in surface water and agricultural soil were examined 360-683 µg/L and 110-266 mg/kg respectively. After calculating the daily intake of As in three age groups (7-15, 16-25 and 26-50 years) it was concluded that 7-15 years age group is at severe risk of arsenicosis than elders through drinking water and usage of grain crops in that district. Nickson et al. [21] analysed 49 subsurface water samples obtained from District Muzaffargarh of Punjab, central Pakistan. Out of 49 well samples, 21 showed below 10 µg/L As and 21 showed greater than 50 µg/L As concentrations. It was also revealed that some wells in urban areas contain less than 50 µg/L As and others contain more than 50 µg/L As levels. In contrast, ground water of rural areas showed less than 25 µg/L of As levels. In addition, As concentrations showed increasing trend with depth and changing geochemical situations.

The surface and subsurface water samples obtained from three areas (Alpuri, Jeejal-Dubair, Besham) of Kohistan region, Pakistan were analysed [22]. Among three regions, ground water samples collected from Jijal-Dubair area showed highest As<sup>3+</sup>, As<sup>5+</sup> and total As concentrations which were 12.27, 4.42 and 16.69 respectively. The study by [33] presented As, fluoride and sulphur levels in Lahore and Kasur districts, Punjab, Pakistan. Authors considered 24 ground water and 5 rainwater samples. The As levels in ground water samples were observed between 32 and 1900 µg/L. The main finding was presence of As, fluoride and sulphur isotopes in rainwater as a result of air pollution. The authors in [30] described noticeable high level of As in the River Ravi which was 9.85 mg/L. The statistical analysis of heavy metals in the ground and surface water of Haripur basin, Pakistan is presented in [29].

The people in Thar Desert of Pakistan utilize fresh and stored rain water for drinking and irrigation. The change in quality of rain water and its correlation to geological conditions, physical parameters, chemical composition, total and inorganic species of As is analyzed in study [25]. The value of As in Thar Desert was found to be 20-70 times greater than WHO acceptable limit.

Baig et al. [4] reported high level of As in the ground and surface water resources of Jamshoro Sindh, Pakistan due to higher saturation of salts in this steppe climate area. The considerably higher concentration of As in ground water compared to surface water was the result of anthropogenic and geothermal factors. Ali et al. [34] suggested that power generation via coal was a vital anthropogenic factor for As elements and combustion process of coal released more than 88.5% of As into the environment.

#### 4. METHODOLOGIES FOR ARSENIC REMOVAL

As removal methods from water include (i) Pre-oxidation of arsenite to arsenate, (ii) adsorption techniques, (iii) Membrane methods, (iv) point-of-use methods (coagulation/adsorption/precipitation/filtration, oxidation/coagulation/filtration/precipitation, oxidation/adsorption/filtration), (v) adsorption/filtration and (vi) biological As removal [35].

#### 4.1 Pre-oxidation of arsenic (III) to arsenic(V)

As is present in nature in different physio-chemical conditions and oxidation numbers. It is present in natural waters in inorganic form of As (+3 and +5). The thermodynamically balanced form of inorganic arsenic is As (V) [36]. As (III) as arsenites compounds are non-ionic and are not always readily removed from potable water. These compounds are first converted into As(V) or arsenates which are ionic at potable water pH to efficiently treat from potable water to safe levels [35].

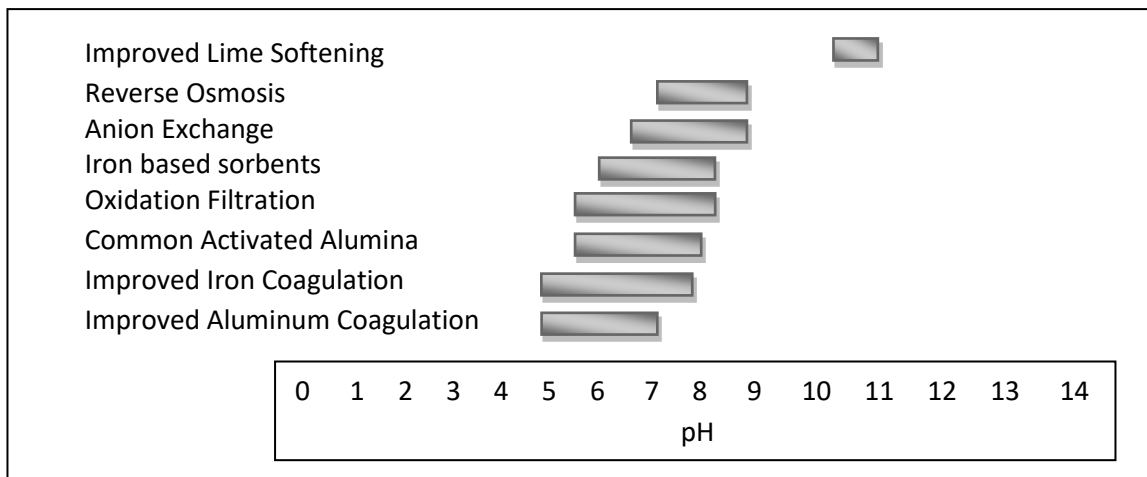


Figure 1. Best possible pH ranges for numerous As treatment methods [37].

The processes which are suitable for removal of anions (such as activated alumina adsorption and anion exchange) are effective for treatment of arsenate but not for arsenite. Other effective methods for treatment of As(V) anions are iron coagulation followed by filtration or microfiltration. Water treatment with metallic iron ( $\text{Fe}^0$ ) confirms the assertion that  $\text{Fe}^0$  is a reducing agent [38]. Iron-oxide-based adsorbents such as granular ferric hydroxide (GFH) and iron-doped filtration as adsorption media are effective. Most of the As removal methods must employ pH adjustment for optimal results and are suitable for treating As(V) state and therefore consist of an oxidation step as pre-treatment to convert As(III) to As(V). Fig. 1 gives a summary of best possible pH ranges for numerous As treatment methods.

#### 4.2 Precipitation and coagulation methods

The methods for As removal from contaminated water rely on the co-precipitation of soluble arsenates on the inorganic oxides of other metals [39] which is now common process to eliminate As from water by using ferric salts or alum as the coagulant. As-bearing coagulates from electrolytic coagulation are usually very fine. Ferric sulfate when used as the coagulant at pH 5 results in formulation of 0.5 to 4 mm particles in size with irregular shape. Such coagulates contain both fine and coarse particles [40]. The scientists [41], proposed coagulation process for As removal from water consisting of four steps: electrolytic coagulation, coating, adsorption, and sedimentation.

*Coating:* The small coagulates generated in the electrolytic coagulation step coat a coarse mineral on the surfaces, forming much larger coagulates that is a mixture of colloidal particles and coarse mineral particles. The minerals used in this step should be charged positively in a wide pH range. In other words, the PZC (point of zero charge) of the mineral should be at a high pH, such as calcite. Therefore, the coating could be realized through electrostatic attraction between the small negatively charged coagulates and the coarse positively charged mineral. The particle size of the mineral could be in the 38–150  $\mu\text{m}$  range. Clearly, the coarser the mineral particles, the larger the mixed coagulates.

*Adsorption:* As(V) adsorbs on the coagulates through chemical adsorption. The As(V) is concentrated on the coarse mineral particles together with the small coagulates.

*Sedimentation:* Since the As-bearing coagulates settle down together with the coated coarse particles, they would have a very high velocity of sedimentation. Accordingly, a low-cost water/solid separation method, sedimentation, would be effective in removing the As-bearing coagulates from contaminated water, producing clean water.

#### 4.3 Nanofiltration

The effective pore sizes of Nanofiltration (NF) membranes range from less than 1 nm to a few nanometers, and by molecular weight cut-off between reverse osmosis and ultrafiltration membranes [42]. The NF membranes are charged either negatively or positively, due to dissociation of functional groups of membrane. Therefore, the separation principles of NF include steric exclusion for neutral species, or steric and charge exclusion between inorganic ions and the membrane, and consequently, different models have been proposed to describe NF membranes processes. The rejection rate for As(V) was subjective to the operating conditions such as operating pressure, initial arsenate concentration, ionic strength and pH. After investigations, the As(V) rejection of the DK membrane was slightly more than the DL membrane for all the operating conditions. It was observed that an increase of operating pressure, initial As(V) concentration and pH verified a privileged competence of As(V) rejection for both membranes, whereas an increase of ionic strength reduced the As(V) rejection [42].

As in water could be treated from 50 to 10 ppb i.e. WHO standard level by coagulation method using 1.50 mg Al/Lit Poly-aluminum chloride  $[Al_2(OH)_nCl_{6-n}]_m$  ( $1 \leq n \leq 5$ ,  $m \leq 10$ ). Nano-filtration (NF) membrane exhibit encouraging results (up to 95%) of As (V) removal at lower working pressure (less than 1 MPa). This membrane also shows promising results of above 75% As (III) removal without using any chemical agents. The researchers recommend the NF membranes for As (III and V) treatment from any kind of source water [36].

#### 4.4 Ion Exchange

The ion exchange media [43] is usually packed into a column. As contaminated water is passed through the column and contaminants are eradicated by reversible displacement ion adsorbed on the solid surface. Numerical simulations were applied to observe the impact of process configuration on ion exchange of As(V). Model parameters were resolved utilizing distributed information on As expulsion from polluted waters by hydrous ferric oxide (HFO) substances and solid anion exchangers (SBA) [44]. A recent study by [45] assessed the attainability of utilizing a particle trade film donnan dialysis based procedure with another methodology of employing sulphate as driving counter-particle for arsenate expulsion from drinking water containing sulphate.

#### 4.5 Reverse Osmosis

Reverse osmosis is one of the effective method of As treatment reported in literature [46]. Reverse osmosis (RO) process may give higher arsenate (V) removal rates as compared to arsenite (III). As (III) compounds could be removed by increasing the pH i.e. by caustic injection to reverse osmosis feed water. The pilot scale studies shows the As removal of 40-99% by reverse osmosis technique. US-EPA published a report that reverse osmosis is an efficient As removal technology by bench and pilot scale methods[47]. In a study by [48] As removal efficiency was compared between nanofiltration and reverse osmosis membranes. The scientists discovered that RO membranes have higher As (III) removal rate than nanofiltration membranes. From the operational point of view pressure of 4 bar is adequate to get 97 - 99 percentage As(III) removal from reverse osmosis membranes.

#### 4.6 Adsorption method

One of the effective method to treat dissolved As is adsorption by materials such as iron oxides, activated carbon and aluminum oxides as these materials have good attraction towards As. These adsorbents powerfully pull As atoms to their sorption areas and ultimately separate As from the solution. The researchers perform laboratory experiments on batch scale with these adsorbents whereas adsorbent packed column are also frequently used. Operationally As polluted water flows through the packed column, where toxic As is captured on the surface of adsorbent. Once the adsorbents are saturated this media could be recharged by smooth procedure [49]. Thirunavukkarasu et al. used iron oxide-coated sand filtration to accomplish less than  $5 \mu\text{g L}^{-1}$  As in drinking water. In a recent study water treatment residuals containing iron (Fe) and manganese oxides were employed as As removal adsorbent from water. These adsorbents show high adsorption capacity of nearly 150 mg As(III) per gm and about 100 mg As(V) per gm. This adsorption process allows As(III) treatment from acidic solution with higher efficiency [1]. Sugarcane bagasse (SCB) removed up to ~98 % of arsenic in water with uptake capacities yield of batch experiment around 11.9 mg/g at pH ~9 [50]. The authors [51], have prepared a novel iron Chitosan nanoparticle (CIN) for As removal from groundwater obtained from Kanpur district, India. Experiments exhibited that CIN is able to efficiently remove As(III) and As(V) with capacity of 119mg/g and 94mg/g respectively. It was found that factors such as sulfate, phosphate ions have minimum effect on the adsorption process. CIN can be recycled five times without alteration in adsorption capacity covering the wide range of pH. The As removal from industrial wastewater using magnetic particles was explored in Iran. The adsorption efficiency of the adsorbent is extremely based on pH and the most favourable pH is 7 for adsorption of As(III). From the experiments it was concluded that by rising the concentration of magnetic nanoparticles, As(III) removal efficiency was improved [52].

The researchers [53] reported that anatase titanium dioxide adsorbent showed higher adsorption capacity for wide range of As concentration. Rutile polymorph of TiO<sub>2</sub> worked efficiently for the removal of As as the solution pH was increased gradually. The authors reported that sunlight and UV light assisted in the As(III), As(V) removal.

The scientists [54] examined four laterite samples from different geographical locations of India and used them for As adsorption. The Langmuir and Freundlich isotherm experiments with 1000 µg/L initial concentrations of As(V) results in 59.2, 75.0, 543 and 365 µg/L final concentrations with four laterite samples. Similarly, experiments with 1000 µg/L initial concentration of As(III) yields 70.1, 89.0, 567 and 465 µg/L final concentrations with four laterite samples. The effects of major minerals such as silicon oxide, iron aluminium, silicate, iron oxide, aluminium silicate, gibbsite etc on As adsorption were also analyzed.

Pandey et al. [55] studied a biomass obtained from *Momordica charantia* that was used for As(III) adsorption from contaminated drinking water. The optimistic parameters were pH (2 to 10), contact (shaking) time (5 to 150 min), adsorbent dosage for metal adsorption (1 to 50 gm/L), initial As (III) concentration (0.10-100 mg/L) etc. It was revealed that biomass was a potential sorbent for 0.5 ppm As (III) with 88% sorption efficiency.

Authors [56] studied the biosorption capacity of rice polish for As removal from aqueous solution. The pH and preliminary metal ion concentration showed direct effect on sorption of As via rice polish. The highest sorption capacity was found to be 138.88 µg/g for As(III) and 147.05 µg/g for As(V).

The adsorption potential of *Salvadora persica* stem ash for the removal of As (V) was reported by [57]. During the first 20 min of batch experiments, the adsorption capacity of *Salvadora persica* stem ash rose rapidly and continued to increase at a slow rate till the equilibrium state was achieved after 80 and 60 min at 300°C and 500°C. The macropore surface of the ash presented quick adsorption and micropore surface of the adsorbent showed slow adsorption because of the surface diffusion process. With the initial concentration of 50-500 µg/L, the stem ash was able to eradicate up to 99% of As(V) from aqueous solutions.

The significant parameters regarding As elimination experiments accomplished in Asian countries have been discussed and results are demonstrated in Table 2. Further, in Table 2, treatment method used for As elimination is shown in the first column, adsorbent is indicated in the second column, the initial and final concentrations of As are illustrated in third and fourth columns respectively. The optimal pH is shown in the fifth column, feasible temperature is presented in the sixth column, models used to calculate the adsorbent capacity is demonstrated in seventh column and contact time is specified in eight columns. Finally the last column specifies the reference of the study.

Table 2. Comparative evaluation of various treatment methods and low-cost adsorbents for Arsenic removal in Asian Countries

Treatment Method	Adsorbent	Initial (As) Conc.	(As) Conc./ removal% after treatment	pH	Temp:	Model used to calculate Adsorbent capacity	Contact Time	Reference
Adsorption	<i>Salvadora persica</i> stem ash	500 µg/L As(V)	< 10 µg/L	6	300 °C and 500 °C	Langmuir and Freundlich isotherm	80 and 60 min	[57]
Nanofiltration	Self-made PMIA asymmetric nano filtration membrane	100 µg/L As(V)	10 µg/L	7	25 °C	–	–	[58]
Adsorption	magnesia-loaded fly ash cenospheres (MGLC) and	50-50000 µg/L		MGLC pH 3.0-8.0 and	298K	Langmuir and	MGLC 120 min	[59]

	manganese-loaded fly ash cenospheres (MNLC)	As(V)	–	MNLC pH 3.0-4.0		Freundlich isotherm	MNLC 60 min	
Adsorption	Chitosan zerovalent Iron Nanoparticle (CIN)	2mg/L As(III) and As(V)	< 5 µg/L	7	25 °C	Langmuir monolayer adsorption	<180 min	[51]
Adsorption	magnetic nanoparticles	10 mg/L As(III)	82%	7	22.5 °C	Freundlich isotherm	20 min	[52]
Adsorption	using 3-[2-(2-aminoethylamino) ethylamino]propyl-trimethoxysilane functionalized silica gel	100 mg/L As(V)	–	2.7-9.2	25 °C	Langmuir and Freundlich isotherm	5-60 min	[60]
Adsorption	Two types of nano TiO <sub>2</sub> crystals	200 ppm As(III) or As(V)	–	4-10	25 °C	Freundlich equations	–	[53]
Batch Adsorption	Four different treated laterite	1000 ppb As(III) and As(V)	–	7± 3	305K	Langmuir and Freundlich isotherm experiment	–	[54]
Batch Adsorption	Biomass from Momordica charantia	0.5 mg/L of As( III)	88% sorption efficiency	2-11	–	Langmuir and Freundlich adsorption isotherm	5-150 min	[55]
Biosorption	Rice Polish	1000 µg/L As(III) and As(V)	0.139 As(III) and 0.147 As(V)	7.0 4.0	20 °C	Langmuir, Dubinin–Radushkevich (D–R) and Freundlich isotherm models	10-150 min	[56]
Nanofiltration and Reverse Osmosis	Thin film polyamide nanofiltration and reverse osmosis membranes	100 µg/L As(III)	97-99%	3.5, 5, 7.5, and 10	45 °C			[48]

#### 4.7 Low cost indigenous arsenic removal technologies from drinking water in Pakistan

To address arsenic removal from water, a number of studies have presented indigenous As removal technologies involving biosorption and adsorption processes for efficient remediation of As from water in Pakistan [4, 17, 23, 35, 61-63]. The major parameters related to those experiments are briefed in Table 3.

Most of the available remediation technologies are based on adsorbents, which have a limited capacity to remove As and needs to be replaced or regenerated. This is possibly one of the major reason for failures of these technologies besides economic viability [64]. Baig et al. [23] investigated the effect of stem of *Acacia nilotica* for As removal from surface water accumulated from lake, canal and river in the Jamshoro district, Sindh, Pakistan. During the biosorption process *Acacia nilotica* showed the 95% sorption efficiency with a concentration of < 200 µg/L of As and its uptake capacity was 50.8 mg/g. Authors in study [65] explored the removal of As(III) and As(V) using titanium dioxide (TiO<sub>2</sub>) nanoparticles. The effects of three types of adsorbents: pure, iron-doped TiO<sub>2</sub> nanoparticles and sand coated with TiO<sub>2</sub> nanoparticles were evaluated along with a broad array of pH. Adsorption potential of TiO<sub>2</sub> nanoparticles was improved by iron doping under different air and light conditions. Experiments confirmed that among the three types of adsorbents used, sand coated with TiO<sub>2</sub> nanoparticles has the highest adsorption capacity. One of the economical adsorbent for elimination of As(III) and As(V) is banana peel presented by [17]. The adsorption capacity of banana peel was tested for ground water samples collected from diverse regions of Sindh. An interesting finding about banana peel adsorbent was its independence with pH which is dissimilar to other studies. The study [66] reported that adsorption of As(III) using tea waste was dependent on pH. The stated adsorption potential of tea waste for Langmuir and Freundlich isotherms was 6.402 mg/g and 4.7424 mg/g respectively. Results showed that As sorption is decreased by increasing the temperature and it increased by rising adsorbate concentration. The maximum sorption of 92.5% was noticed at 10ppm concentration of tea waste. Authors in study [63] examined Chir pine leaves commonly available in northern Pakistan and proved it an excellent adsorbent for As(V) removal from water. Effect of pH, contact time and agitation speed on the adsorption of As (V) are also analysed. The highest adsorption capacity of pine leaves was observed to 3.27 mg/g at pH 4.0, contact time 35 min at 25°C. Adsorption method for As treatment is getting a lot of interest by researchers as compared to other methods. This technique gives good results, proves to be more effective because of its simple design with operational conditions and economics. In a study [67], authors found that hydrated Portland cement, marble powder and bricks powder exhibits above 90% As removal from solution of 1 mg/L with contact time of 1 hour at neutral pH and dosage of 30 gm/L.

Table 3. Comparative evaluation of various treatment methods and low-cost adsorbents for arsenic removal in Pakistan

Treatment Method	Adsorbent	Initial (As) Conc.	(As) Conc./ removal % after treatment	pH	Temp	Contact Time	Efficiency (%)	Cost of adsorbent	Reference
Biosorption	stem of <i>Acacia nilotica</i>	200 µg/L	< 10 µg/L	7.5	298-318K	15 min	95	USD 0.10 per Kg	[23]
Adsorption	Titanium dioxide	100 µg/L	95%	As(III) 1-2 As(V) 7	-	-	95	\$3.5 per Kg	[65]
Adsorption	Banana peel	As(III) and As(V)	95%	Independent of pH	25±0°C	30 min	98	Low cost, locally available	[17]
Adsorption	Tea waste	As(III)	92.5%	7	25°C	100 min	92.5	Low cost material	[66]
Adsorption	Pine leaves ( <i>Pinus roxburghii</i> )	10 mg/L As(V)	-	4.0	25°C	35 mins	92.4	Low cost, available tree	[63]
Adsorption	Orange Peel	As(V)	-	7	25°C	2 hrs	85	Low cost, locally grown fruit	[68]

## 5. RESULTS AND DISCUSSION



As exposure through drinking water contamination is worldwide problem which causes severe health hazards to humans. A number of diverse treatment technologies presented in literature could diminish arsenic concentrations to satisfactorily lower levels; however developing countries are unable to address this issue because most of the commercially viable As removal technologies are unsuitable for rural communities in developing countries where centralised water treatment facilities are frequently absent. High cost of commercial As removal technologies are also hindering the wide scale adoption [69]. Developing countries are still looking for viable, simple, inexpensive technologies to facilitate rural areas where running water or electricity are unavailable [70]. Such As removal technology should be simple and affordable which can be carried out at household level [71].

Among various As removal technologies, adsorption is a fast, economical and widespread method. One of the valuable home practices is the treatment with metallic iron which is followed by simple decantation. Materials with high metal (Fe, Al, Cu) content or metal-coated materials demonstrated the highest As adsorption potential. Researchers are continuously exploring low-cost indigenous adsorbents. Mohan et al. reviewed the sorption capacities of various adsorbents [72]. The sludge-free nature adsorption technologies make them suitable for low skilled communities [2]. Several low-cost adsorbents investigated worldwide for As removal showed better performance includes treated slags, carbons obtained from agricultural waste, biosorbents (immobilized biomass, orange juice residue), goethite and some commercial adsorbents, which include resins, gels, silica, treated silica. Amongst all these adsorbents; immobilized biomass adsorbents presented exceptional performances [72].

Clays, sand, silica, etc. are economical universally available adsorbents, but these possess lower As adsorption competence than the majority of the adsorbents [72]. Iron oxides and oxy-hydroxides belongs to appropriate categories of adsorbents for As removal because of their adsorption competence, strong binding with adsorbed As and low-price [73]. Iron or iron compounds [iron oxides, oxyhydroxides and hydroxides, including amorphous hydrous ferric oxide (FeO-OH), goethite ( $\alpha$ -FeO-OH) and hematite ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>), etc. are amongst the most extensively used adsorbents, encompassing privileged removal efficiency. Iron-based sorbents also represent a promising treatment technology for As removal [72]. Batch and column studies by authors [74] found ironoxide-coated sand filtration achieved less than 5 µg/L As in drinking water.

## 6. CONCLUSION

A lot of research has been conducted to measure As concentrations in different regions of the world and to reduce the As concentrations over the past decades. In this study an attempt has been made to summarize selected information of As contaminations in Pakistan along with As removal techniques. The current facts and figures related with water contamination by As in Pakistan emerge alarming situation which need to be focused by researchers for feasible provision of water safety. Various low cost materials have been investigated for As removal from the water, however; challenges such as straightforward practices for development at local communities, adequate accessibility, and elevated removal effectiveness on real groundwater conditions such as the subsistence at neutral pH are still existing. Different studies have identified iron or iron compounds [iron oxides, oxyhydroxides and hydroxides, including amorphous hydrous ferric oxide (FeO-OH), goethite ( $\alpha$ -FeO-OH) and hematite ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>), etc. as novel household drinking water treatment device for As removal. However, further studies to evaluate the As removal efficiency on real groundwater conditions such as the existence at neutral pH are still sturdily needed.

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## 8. REFERENCES

- [1] D. Ociński, *et al.*, "Water treatment residuals containing iron and manganese oxides for arsenic removal from water—Characterization of physicochemical properties and adsorption studies," *Chemical Engineering Journal*, vol. 294, pp. 210-221, 2016.
- [2] S. A. Baig, *et al.*, "Arsenic Removal from Natural Water Using Low Cost Granulated Adsorbents: A Review," *CLEAN – Soil, Air, Water*, vol. 43, pp. 13-26, 2015.
- [3] B. K. Mandal and K. T. Suzuki, "Arsenic round the world: a review," *Talanta*, vol. 58, pp. 201-235, 8/16/2002.
- [4] J. A. Baig, *et al.*, "Evaluation of arsenic and other physico-chemical parameters of surface and ground water of Jamshoro, Pakistan," *Journal of hazardous materials*, vol. 166, pp. 662-669, 2009.
- [5] H. V. Aposhian, *et al.*, "Urinary excretion of meso-2,3-dimercaptosuccinic acid in human subjects," *Clinical Pharmacology & Therapeutics*, vol. 45, pp. 520-526, 1989.

- [6] Y. Chen, *et al.*, "Arsenic exposure at low-to-moderate levels and skin lesions, arsenic metabolism, neurological functions, and biomarkers for respiratory and cardiovascular diseases: Review of recent findings from the Health Effects of Arsenic Longitudinal Study (HEALS) in Bangladesh," *Toxicology and Applied Pharmacology*, vol. 239, pp. 184-192, 9/1/ 2009.
- [7] C. O. Abernathy, *et al.*, "Health Effects and Risk Assessment of Arsenic," *The Journal of Nutrition*, vol. 133, pp. 1536S-1538S, May 1, 2003 2003.
- [8] I. Ali and V. K. Gupta, "Advances in water treatment by adsorption technology," *Nat. Protocols*, vol. 1, pp. 2661-2667, 01//print 2007.
- [9] M. R. Karagas, *et al.*, "Drinking Water Arsenic Contamination, Skin Lesions, and Malignancies: A Systematic Review of the Global Evidence," *Current environmental health reports*, vol. 2, pp. 52-68, 2015.
- [10] D. E. Giles, *et al.*, "Iron and aluminium based adsorption strategies for removing arsenic from water," *Journal of Environmental Management*, vol. 92, pp. 3011-3022, 2011.
- [11] N. R. Nicomel, *et al.*, "Technologies for Arsenic Removal from Water: Current Status and Future Perspectives," *International Journal of Environmental Research and Public Health*, vol. 13, p. 62, accepted 2016.
- [12] P. L. Smedley and D. G. Kinniburgh, "A review of the source, behaviour and distribution of arsenic in natural waters," *Applied Geochemistry*, vol. 17, pp. 517-568, 5// 2002.
- [13] I. Svalina, *et al.*, "An adaptive network-based fuzzy inference system (ANFIS) for the forecasting: The case of close price indices," *Expert systems with applications*, vol. 40, pp. 6055-6063, 2013.
- [14] T. J. Sorg, *et al.*, "Arsenic species in drinking water wells in the USA with high arsenic concentrations," *Water Research*, vol. 48, pp. 156-169, 1/1/ 2014.
- [15] J. He and L. Charlet, "A review of arsenic presence in China drinking water," *Journal of Hydrology*, vol. 492, pp. 79-88, 6/7/ 2013.
- [16] D. Chakraborti, *et al.*, "Arsenic calamity in the Indian subcontinent: What lessons have been learned?," *Talanta*, vol. 58, pp. 3-22, 8/16/ 2002.
- [17] S. Q. Memon, *et al.*, "Evaluation of banana peel for treatment of arsenic contaminated water," in *Proceedings of the 1st Technical Meeting of Muslim Water Researchers Cooperation (MUWAREC)*, 2008, pp. 104-109.
- [18] A. H. Shar, *et al.*, "Enumeration of total and fecal coliform bacteria in drinking water of Khairpur Sindh," *Pak J Med Res*, vol. 47, pp. 18-21, 2008.
- [19] M. B. Arain, *et al.*, "Determination of arsenic levels in lake water, sediment, and foodstuff from selected area of Sindh, Pakistan: Estimation of daily dietary intake," *Food and Chemical Toxicology*, vol. 47, pp. 242-248, 1// 2009.
- [20] K. D. Brahman, *et al.*, "Evaluation of high levels of fluoride, arsenic species and other physicochemical parameters in underground water of two sub districts of Tharparkar, Pakistan: A multivariate study," *Water research*, vol. 47, pp. 1005-1020, 2013.
- [21] R. T. Nickson, *et al.*, "Arsenic and other drinking water quality issues, Muzaffargarh District, Pakistan," *Applied Geochemistry*, vol. 20, pp. 55-68, 1// 2005.
- [22] S. Muhammad, *et al.*, "Arsenic health risk assessment in drinking water and source apportionment using multivariate statistical techniques in Kohistan region, northern Pakistan," *Food and Chemical Toxicology*, vol. 48, pp. 2855-2864, 10// 2010.
- [23] J. A. Baig, *et al.*, "Biosorption studies on powder of stem of *Acacia nilotica*: removal of arsenic from surface water," *Journal of hazardous materials*, vol. 178, pp. 941-948, 2010.
- [24] G. M. Arain, *et al.*, "A Preliminary Study on the Arsenic Contamination of Underground Water," *Jour. Chem. Soc. Pak. Vol.*, vol. 29, p. 463, 2007.
- [25] K. Brahman, *et al.*, "Evaluation of fresh and stored rainwater quality in fluoride and arsenic endemic area of Thar Desert, Pakistan," *Environmental monitoring and assessment*, vol. 186, pp. 8611-8628, 2014/12/01 2014.
- [26] M. A. Malana and M. A. Khosa, "Groundwater pollution with special focus on arsenic, Dera Ghazi Khan-Pakistan," *Journal of Saudi Chemical Society*, vol. 15, pp. 39-47, 2011.
- [27] J. A. Baig, *et al.*, "Evaluation of arsenic levels in grain crops samples, irrigated by tube well and canal water," *Food and Chemical Toxicology*, vol. 49, pp. 265-270, 2011.
- [28] A. Farooqi, *et al.*, "Toxic fluoride and arsenic contaminated groundwater in the Lahore and Kasur districts, Punjab, Pakistan and possible contaminant sources," *Environmental pollution*, vol. 145, pp. 839-849, 2007.
- [29] S. Jabeen, *et al.*, "Physico-chemical parameters of surface and ground water and their environmental impact assessment in the Haripur Basin, Pakistan," *Journal of Geochemical Exploration*, vol. 138, pp. 1-7, 3// 2014.
- [30] G. Jabeen and M. Javed, "Evaluation of arsenic toxicity to biota in river Ravi (Pakistan) aquatic ecosystem," *International Journal of Agriculture and Biology*, vol. 13, pp. 929-934, 2011.

- [31] A. Farooqi, *et al.*, "Sources of arsenic and fluoride in highly contaminated soils causing groundwater contamination in Punjab, Pakistan," *Archives of environmental contamination and toxicology*, vol. 56, pp. 693-706, 2009.
- [32] J. A. Baig, *et al.*, "Evaluation of toxic risk assessment of arsenic in male subjects through drinking water in southern Sindh Pakistan," *Biological trace element research*, vol. 143, pp. 772-786, 2011.
- [33] K. Khan, *et al.*, "Health risks associated with heavy metals in the drinking water of Swat, northern Pakistan," *Journal of Environmental Sciences*, vol. 25, pp. 2003-2013, 10/1/ 2013.
- [34] J. Ali, *et al.*, "Monitoring of arsenic fate with proximate parameters and elemental composition of coal from Thar coalfield, Pakistan," *Journal of Geochemical Exploration*, vol. 159, pp. 227-233, 12// 2015.
- [35] A. H. Malik, *et al.*, "Perspectives of low cost arsenic remediation of drinking water in Pakistan and other countries," *Journal of Hazardous Materials*, vol. 168, pp. 1-12, 8/30/ 2009.
- [36] Y. Sato, *et al.*, "Performance of nanofiltration for arsenic removal," *Water Research*, vol. 36, pp. 3371-3377, 7// 2002.
- [37] C. K. Jain and R. D. Singh, "Technological options for the removal of arsenic with special reference to South East Asia," *Journal of Environmental Management*, vol. 107, pp. 1-18, 9/30/ 2012.
- [38] M. A. Ali, *et al.*, "Development of low-cost technologies for removal of arsenic from groundwater," *Technologies for Arsenic Removal from Drinking Water. Edited by: M. Feroze Ahmed, M. Ashraf Ali and Zafar Adeel. Bangladesh University of Engineering and Technology, Dhaka-The United Nations University, Tokyo*, pp. 99-120, 2001.
- [39] J. H. Gullledge and J. T. O'Connor, "Removal of arsenic (V) from water by adsorption on aluminum and ferric hydroxides," *Journal / American Water Works Association*, vol. 65, pp. 548-552, 1973.
- [40] D. Fuerstenau, *et al.*, "The recovery of fine particles by physical separation methods," in *Beneficiation of Mineral Fines*, ed: AIME New York, 1979, pp. 3-59.
- [41] S. Song and M. Gallegos-Garcia, "Chapter 11 - Arsenic Removal from Water by the Coagulation Process," in *The Role of Colloidal Systems in Environmental Protection*, M. Fanun, Ed., ed Amsterdam: Elsevier, 2014, pp. 261-277.
- [42] J. Fang and B. Deng, "Rejection and modeling of arsenate by nanofiltration: Contributions of convection, diffusion and electromigration to arsenic transport," *Journal of Membrane Science*, vol. 453, pp. 42-51, 3/1/ 2014.
- [43] M. R. Awual, *et al.*, "Evaluating of arsenic (V) removal from water by weak-base anion exchange adsorbents," *Environmental Science and Pollution Research*, vol. 20, pp. 421-430, 2013.
- [44] M. Laatikainen, *et al.*, "Comparison of ion exchange process configurations for arsenic removal from natural waters," *Desalination and Water Treatment*, pp. 1-12, 2015.
- [45] M. Pessoa-Lopes, *et al.*, "Arsenate removal from sulphate-containing water streams by an ion-exchange membrane process," *Separation and Purification Technology*, vol. 166, pp. 125-134, 2016.
- [46] M. Fidaleo, *et al.*, "Assessment of the energy needs for the arsenic remediation of drinking water by electrodialysis," *Desalination and Water Treatment*, pp. 1-13, 2015.
- [47] R. Y. Ning, "Arsenic removal by reverse osmosis," *Desalination*, vol. 143, pp. 237-241, 2002.
- [48] H. Elcik, *et al.*, "Performance of nanofiltration and reverse osmosis membranes for arsenic removal from drinking water," *Desalination and Water Treatment*, pp. 1-8, 2015.
- [49] K. P. Kowalski, "Chapter 8 - Advanced Arsenic Removal Technologies Review," in *Chemistry of Advanced Environmental Purification Processes of Water*, E. G. Søggaard, Ed., ed Amsterdam: Elsevier, 2014, pp. 285-337.
- [50] H. Tajernia, *et al.*, "Arsenic removal from water by sugarcane bagasse: an application of response surface methodology (RSM)," *Water, Air, & Soil Pollution*, vol. 225, p. 2028, 2014.
- [51] A. Gupta, *et al.*, "Zerovalent iron encapsulated chitosan nanospheres – A novel adsorbent for the removal of total inorganic Arsenic from aqueous systems," *Chemosphere*, vol. 86, pp. 150-155, 1// 2012.
- [52] A. Khodabakhshi, *et al.*, "Synthesis of magnetite nanoparticles and evaluation of its efficiency for arsenic removal from simulated industrial wastewater," *Iranian Journal of Environmental Health Science & Engineering*, vol. 8, pp. 189-200, 2011.
- [53] L. Ma and S. X. Tu, "Removal of arsenic from aqueous solution by two types of nano TiO<sub>2</sub> crystals," *Environmental Chemistry Letters*, vol. 9, pp. 465-472, 2011/12/01 2011.
- [54] A. Maiti, *et al.*, "Comparison of treated laterite as arsenic adsorbent from different locations and performance of best filter under field conditions," *Journal of hazardous materials*, vol. 262, pp. 1176-1186, 2013.
- [55] P. K. Pandey, *et al.*, "Biosorptive removal of arsenic from drinking water," *Bioresource technology*, vol. 100, pp. 634-637, 2009.

- [56] D. Ranjan, *et al.*, "Biosorption of arsenic from aqueous solution using agricultural residue 'rice polish'," *Journal of Hazardous Materials*, vol. 166, pp. 1050-1059, 2009.
- [57] F. Kord Mostafapour, *et al.*, "Arsenic removal from aqueous solutions by *Salvadora Persica* stem ash," *Journal of Chemistry*, vol. 2013, 2012.
- [58] C. Zhao, *et al.*, "Arsenic Removal from Drinking Water by Self-Made PMIA Nanofiltration Membrane," *Advances in Chemical Engineering and Science*, vol. 2, pp. 366-371, 2012.
- [59] Q. Li, *et al.*, "Comparison of two adsorbents for the removal of pentavalent arsenic from aqueous solutions," *Journal of Environmental Management*, vol. 98, pp. 98-106, 5/15/ 2012.
- [60] H.-T. Fan, *et al.*, "Removal of arsenic(V) from aqueous solutions using 3-[2-(2-aminoethylamino)ethylamino]propyl-trimethoxysilane functionalized silica gel adsorbent," *Desalination*, vol. 278, pp. 238-243, 9/1/ 2011.
- [61] J. A. Baig, *et al.*, "Biosorption studies on powder of stem of *Acacia nilotica*: Removal of arsenic from surface water," *Journal of Hazardous Materials*, vol. 178, pp. 941-948, 6/15/ 2010.
- [62] D. Nabi, *et al.*, "Evaluation of the adsorption potential of titanium dioxide nanoparticles for arsenic removal," *Journal of Environmental Sciences*, vol. 21, pp. 402-408, // 2009.
- [63] U. Shafique, *et al.*, "Removal of arsenic from water using pine leaves," *Journal of the Taiwan Institute of Chemical Engineers*, vol. 43, pp. 256-263, 3// 2012.
- [64] S. Chaudhari, *et al.*, "7 - Domestic- and Community-Scale Arsenic Removal Technologies Suitable for Developing Countries," in *Water Reclamation and Sustainability*, S. Ahuja, Ed., ed Boston: Elsevier, 2014, pp. 155-182.
- [65] N. Deedar and I. Aslam, "Evaluation of the adsorption potential of titanium dioxide nanoparticles for arsenic removal," *Journal of Environmental Sciences*, vol. 21, pp. 402-408, 2009.
- [66] M. Shaikh, *et al.*, "Utilization of tea waste for the removal of arsenic (III) from aqueous solution," *Sindh University Research Journal-SURJ (Science Series)*, vol. 43, 2011.
- [67] S. Bibi, *et al.*, "Evaluation of industrial based adsorbents for simultaneous removal of arsenic and fluoride from drinking water," *Journal of Cleaner Production*, vol. 87, pp. 882-896, 2015.
- [68] M. I. Khaskheli, *et al.*, "Use of orange peel waste for arsenic remediation of drinking water," *Waste and Biomass Valorization*, vol. 2, pp. 423-433, 2011.
- [69] C. Noubactep and P. Wofo, "Elemental Iron (Fe0) for Better Drinking Water in Rural Areas of Developing Countries," in *Uranium, Mining and Hydrogeology*, B. J. Merkel and A. Hasche-Berger, Eds., ed Berlin, Heidelberg: Springer Berlin Heidelberg, 2008, pp. 121-130.
- [70] A. Ramaswami, *et al.*, "Batch-Mixed Iron Treatment of High Arsenic Waters," *Water Research*, vol. 35, pp. 4474-4479, 12// 2001.
- [71] B. Petrusevski, *et al.*, "Adsorbent-based point-of-use system for arsenic removal in rural areas," *Journal of Water Supply: Research and Technology-Aqua*, vol. 51, pp. 135-144, 2002.
- [72] D. Mohan and C. U. Pittman Jr, "Arsenic removal from water/wastewater using adsorbents—A critical review," *Journal of Hazardous Materials*, vol. 142, pp. 1-53, 4/2/ 2007.
- [73] P. Mondal, *et al.*, "Laboratory based approaches for arsenic remediation from contaminated water: recent developments," *Journal of Hazardous materials*, vol. 137, pp. 464-479, 2006.
- [74] O. S. Thirunavukkarasu, *et al.*, "Arsenic Removal from Drinking Water using Iron Oxide-Coated Sand," *Water, Air, and Soil Pollution*, vol. 142, pp. 95-111, 2003.