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Chapter

Removal of Arsenic - "A Silent Killer" in the Environment by Adsorption Methods

Ashok Kumar, Kaman Singh, Utkarsh Dixit, Rayees Ahmad Bhat and Satya Prakash Gupta

Abstract

Water is one of the most essential requirements for living being to survive because 70-80% of the mass of most living bodies consists of water and various mineral and organic salts. Water is also most important component of our environment. Large amount of water is used in various industries or commercial level or domestic level and finally effluent water is loaded with large amount of pollutants such as organic chemicals (surfactants, dyes, phenols etc.), inorganic hazardous heavy metals (As in present case) microbes (bacteria, fungi etc.) pollutants particulate etc. Arsenic is a natural metalloid chemical that may be present in groundwater and surface water gets polluted, hence, aquatic life of plants and animals is disturbed and cause abnormal growth and various diseases, hence, short term or long term changes occurs in ecosystem. Hence, treatment of wastewater is essentially required before discharge effluent wastewater into ponds or lagoons, drains and rivers. Arsenic is one such element that contaminates the environment as reported in several countries. The largest population at risk is in Bangladesh followed by India (West Bengal). Arsenic is familiar as silent killer because dissolved in water, it is colorless, odorless, and tasteless, yet consumption of relatively small doses of this element in its most toxic forms can cause rapid and violent death. It is a human carcinogen in water over a wide range of pH values, having harmful effects on both human health and environment, even at low concentration. Because of this effect, the World Health Organization (WHO) and the US Environmental Protection Agency (USEPA) set the arsenic standard for drinking water at .010 ppm to protect consumers served by public water systems. Ingestion only poses health problems if a dangerous amount of arsenic enters the body. Then, it can lead to cancer, liver disease, coma, and death. There is no effective treatment for arsenic toxicity. Only the removal of arsenic from aqueous system can prevent the toxicity. A great deal of research over recent decades has been done to lower the concentration of arsenic in drinking water and still there is a need to develop ecofriendly techniques. Existing major arsenic removal technologies include oxidation, adsorption, precipitation, coagulation and membrane separation. This book chapter presents a systematic description of current status of research in the area of arsenic removal from contaminated water and comparison of all technologies available with more emphasis on adsorption.

Keywords: Arsenic, Adsorption, Environmental and Health Aspects

1. Introduction

Water is one of the most essential requirements for living being to survive because all physiochemical processes of body require aqueous medium this is due to Moreover, 70–80% of the mass of most living bodies consists of water and various mineral and organic salts [1]. Large amount of water is used in various industries or commercial level or domestic level and finally effluent water is loaded with large amount of pollutants such as organic chemicals (surfactants, dyes, phenols, etc.), inorganic hazardous heavy metals (As, Hg, Cd, Pb, etc.) microbes (bacteria, fungi, etc.) pollutants particulate etc. Arsenic is a natural metalloid chemical that may be present in groundwater and surface water gets polluted, hence, aquatic life of plants and animals is disturbed and cause abnormal growth and various diseases, hence, short term or long term changes occurs in ecosystem [2–4]. Very low concentration (1.50 mg/L) of surfactant is lethal for microorganism, even about 0.50 mg/L is harmful for aquatic life. For human life limit of anionic surfactant concentration should up to 1.0 mg/L. High concentration of surfactant in drinking water causes cancer, irritation, dermatitis, eyes disorder. Water has a broad impact on all aspects of human life including but not limited to health, food, energy, and economy. In addition to the environmental, economic, and social impacts of poor water supply and sanitation, the supply of fresh water is essential for the safety of children and the poor. It is estimated that 10.0–20.0 million people die every year due to waterborne and nonfatal infection causes death of more than 200.0 million people every year. Every day, about 5,000.0-6,000.0 children die due to the water-related problem of diarrhea. There are currently more than 0.78 billion people around the world who do not have access to safe water resources resulting in major health problems [5]. Hence, it increases the permeability of cell membrane, and hence, removal of these pollutants are necessary from industrial and household water [6].

Release of hazardous pollutants and their dispersal in the environment can cause adverse impacts on the environment and to public health [7]. These pollutants are more easily controlled when they are generated than after they are dispersed. It is therefore of prime necessity to design treatment processes that isolate and remove the contaminants at their source [8]. Various methods have been developed in the past decades for treatment of waste water for arsenic as biological, physical and chemical methods. In these methods includes chemical precipitation, flocculationcoagulation [9], electro-flotation, electrochemical destruction, electrochemical coagulation [10], biological degradation [11], ozonation, hydrogen peroxide [12], reverse osmosis [13] etc. All these methods are good but have limited applications and all are very expensive, hence, could not use by small industry for wastewater treatments. For that reason there is need for some conventional method which are economically and ecofriendly for wastewater treatments (As in present case). Adsorption is one of the most extensively applied techniques for the removal of pollutants from the industrial effluents. The prominent and emerging trend of subjecting biosorbents in the adsorption technology is mainly because of their natural existence, abundance, renewable, biodegradable and economic features. The adsorption isotherm equations used to describe the experimental data and the thermodynamic assumptions of the various models [14–17].

2. Distribution of arsenic in various parts of world water bodies

In the nature arsenic element is found in soil, water and sediments as arsenic oxides. The common chemical oxidation of arsenic in the nature are -3, +3, 0 and +5.", etc. According to the national agency for the research of cancer

Water type	As contamination (µg/Liter)	Ref.
Ground water in various part of world	1 -73.6	[19]
US Rivers	0.1-2	[20]
Gomti River, India	1.29-9.62	[21]
Manchar Lake, Pakistan	60.45	[22]
Alpine River, France	0.1-263	[23]
Zenne River, Belgium	0.1-263	[24]

Table 1.The distribution of arsenic in natural water can be given as below.

arsenic compounds are put in group 1 carcinogens [18]. According to World Health Organization the maximum contaminant level of arsenic in the drinking water should not be greater than 10 μ g/liter. By the dissolution of minerals, microbial activity arsenic can release into the aquatic environment. Living organism can be affected by arsenic through drinking water. Arsenic polluted water causes damage to central nervous system, kidney, liver, lungs and skin in humans. Further chronic arsenic can cause cardio diseases, hypertension and affects vascular system. Long use of arsenic contaminated water can also cause pigmentation of skin, development of hard paths on the palm of humans. Therefore removal of arsenic from waste water has been remained a subject of concern (**Table 1**) [17, 18].

3. Arsenic removal by adsorption

Many methods have been given for Arsenic removal which include chemical precipitation [25], adsorption [26], ion exchange [27], reverse osmosis [28], and electro-dialysis [29]. Out of all these methods adsorption method found to be cheap and best for the removal of arsenic. There are many kinds of adsorbents available for arsenic removal, for their convenient study we can divide them in two categories. The first category is metal and its alloys such as manganese oxide, activated alumina and iron compounds; the second category is activated carbon obtained from red mud, coconut shell and other carbon-like materials. Larger is the surface area of the adsorbent, stronger is its adsorption effect. It is found that that adsorption of As(V) is better than As(III) (Figure 1).

3.1 Adsorption isotherm models

3.2 The selection of isotherm models

The Akaike information criterion is used for the selection of appropriate model under the situation of when data fitted by more than one model. The Akaike information criterion is represented as below [30].

$$AlC = 2k - 2\ln(L)$$

Where k is the number of parameters in the model and L is the maximum value of the likelihood function for the model.

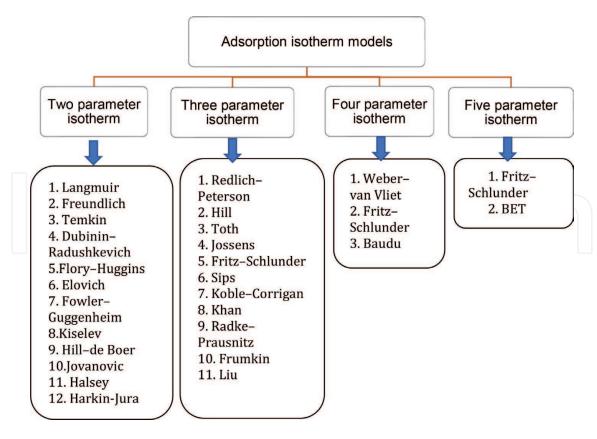


Figure 1.Different adsorption isotherm models used to describe the experimental data and the thermodynamic assumptions of adsorption method.

3.3 Arsenic removal by iron based adsorbents

Iron based adsorbents are extensively developed and used for the removal of arsenic from water [31] (**Table 2**). Some adsorbents such as granular ferric hydroxide (GFH) and zero-valent iron have been produced on an industrial scale as

Adsorbents	Surface area (m ² g ⁻¹)	Initial concentration (mg L ⁻¹⁾	рН	Adsorption capacity (mg g ⁻¹) As(III)	Adsorption capacity (mg g ⁻¹) As (V)	Ref.
Granular ferric hydroxide (GFH)	240–300	As(V):0.1	6.5-7.5		1.1	[32]
α-FeOOH nanoparticles	167.8	As(V):100	3.0	-	76	[33]
Ultrafine Fe2O3 nanoparticles	162	_	4.0	47	95	[34]
Ultrafine FeOOH	135	As(V): 20	7.0	_	37.3	[35]
β-FeOOH nanoparticles	330	As(V): 20	7.5	_	120	[36]
Magnetite- magnetite nanoparticles	49	As(III): 1.5 As(V): 1.5	2.0	3.69	3.71	[37]
γ -Fe2O3 nanoparticles	41-49	As(V): 1	7.0	_	2.9	[38]

Table 2.Different iron compounds used as adsorbent for As(III) and As(V) adsorption from aqueous system.

commercial adsorbents [39]. Iron oxy-hydroxides are mostly used as the adsorbent because of their easy accessibility. The commonly used iron oxy-hydroxides such as, akaganeite (β -FeOOH), goethite (α -FeOOH), lepidocrocite (γ -FeOOH), ferrihydrites (Fe₁₀O₁₄(OH)₂), green rusts can be chemically synthesized by the precipitation of Fe(III) or Fe(+2) salts through the hydrolysis and oxidation processes [40].

3.4 Adsorption of arsenic using activated carbon (AC)

Activated carbon is the most effective and efficient and most widely used because of its versatile nature and convenient for removal of As(III) and As(V). The activated carbon is micro-porous form of the carbon having large surface area and greater number of pores [41]. Arsenic metal cannot be removed completely by simple chemical or physical treatments. So, in this case, AC is used to remove the toxic metals completely from aqueous solution because there is formation of surface complexes between acidic surface functional groups of AC and the metal ions [42]. The removal efficiency is dependent on various factors, like solution concentration initial pH, ionic strength, adsorbent modification methods, nature of adsorbate, chemical nature of AC, and physical properties (surface area, porosity) [43–45]. Adsorption of both arsenic is largely affected by environmental factors such as pH solution, ionic strength, and coexisting substances such as anions, cations, and organic matter. The adsorption capacity of the adsorbents depends not only on the surface area, pore volume, and particles size but also on a combination of all factors, surface chemistry, and pore structure. Specific area of the adsorbents does not contribute to the adsorption capacity on the removal of arsenic from water. Therefore selection of the adsorbents for removal of arsenic should be based on a combination of all factors for the adsorbents and adsorbate.

3.4.1 Preparation of adsorbents

There are two different methods for preparation of activated carbon one is physical and other one chemical. Chemical activation is better than physical because it requires lower temperature and global yield is more since burn-off does not require (**Figure 2**) [45].

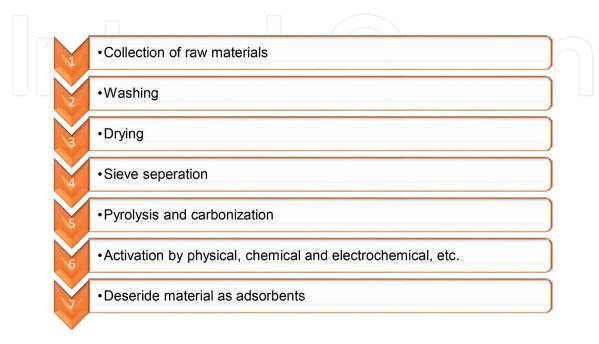


Figure 2.General flow diagram for the preparation of adsorbents.

Adsorbents	Surface area (m ² g ⁻¹)	Initial concentration (mg/L)	pН	Capacity As (III) mg/gm	Capacity As (V) mg/gm	Isotherm model fitted	Ref.
Coconut husk	206	50-60	12	146.30	_		[46]
Coconut shell with 3% ash	1150-1250	0-200	6	_	2.4	Langmuir	[47]
Ce-Ti oxide adsorbent	137.4	50	6.5	7.5		Langmuir	[48]
Fe ₃ O ₄ loaded activated carbon	349	200	8	_	204.2	Freundlich	[49]
Char Carbon	36.48	157-992	2-3	89	34.46	V	[50]
Red mud	130	7.5-220	4.5	0.541	7.642	_	[51]
Pine Leaves	(\bigcirc)	10	4	_	3.27	Both Langmuir and Flory-Huggins	[52]
Oat Hulls	520	25-200	5	_	3.09	Langmuir	[53]
Iron Impregnated GAC	650	0-5	7	_	1.95	Langmuir	[54]
AC (apricot stone)	1547	4.5	_	_	0.034	Both Freundlich and Dubinin–Radushkevich	[55]
Fe (II) loaded	1231	4.5	3	_	2.023	Redlich–Peterson	[56]
Fe (III) loaded	987	4.5	3	_	3.009	Redlich-Peterson	[57]
Sugar beet pulp	821	0-5	9.1-9.4	_	0.691	Langmuir	[58]
Sugar beet pulp-Fe	762	0-3.5	8.5-9.1	_	2.9	Langmuir	[59]
Empty fruit bunch biochar	1890	3-300	9.4	18.9	5.5	Langmuir	[60]
Rice husk biochar	25.16	3-300	8.5	19.3	7.1	Langmuir	[61]
Fe coated empty fruit bunch biochar	(QD)	3-300	9.4	31.4	15.2	Both Langmuir and Freundlich	[62]
Fe coated rice husk biochar		3-300	8.5	30.7	16	Langmuir	[63]
Leonardite char	65.68	1-80	7	4.46	8.40	Langmuir	[64]
Tea Waste		1-100	7	189	154	Langmuir	[65]

Adsorbents	Surface area	Initial	pН	Capacity As (III)	Capacity	Isotherm model fitted	Ref.
	$(\mathbf{m}^2 \ \mathbf{g}^{-1})$	concentration (mg/L)		mg/gm	As (V) mg/gm	7	
Concrete Sludge	23	10-700	7	_	175	Langmuir	[66]
Chitosan	3.1	0.025-2	5.6-6.2	_	0.73	Langmuir	[67]
Iron- Chitosan flakes	1.44	1-10	7	16.2	22.5	Langmuir	[68]
Iron- Chitosan granules	96.8	1-10	7	2.32	2.24	Langmuir	[69]

Table 3.Different adsorbents and their adsorption capacity for the effective removal As(III) and As(V) employing various adsorption isotherm models.

4. Adsorbents comparison

The adsorption capacity of various adsorbents for the effective removal arsenic employing various adsorption isotherm models have been summarized in **Table 3**.

5. Characteristics of various methods for the removal of arsenic from aqueous system

In order to improve the current analytical methods by removing or treating arsenic from aqueous system, a number of methods have been developed and reviewed in this chapter, which included several method with their characteristics properties (**Table 4**).

Such information should be taken into consideration in order to improve the current methods or develop new advanced methods. The best analytical methods for aresenic speciation are considered those, including chromatographic separations based on adsorption coupled with a sensitive detection system. Specific sorbents and exchange resins have been developed and applied recently for this purpose. Apart from the chromatographic and non-chromatographic methods for the arsenic

Method	Method in detail	Characteristics	Ref.
Physical	Mixing both contaminated and uncontaminated soils	High cost/usage to smaller- scale operations	[70–72]
	Washed with sulfuric acid, nitric acid, phosphoric acid, and hydrogen bromide	Chemicals usage/high cost/usage to smaller-scale operations	
	Immobilize soluble arsenates using cement	Successfully used to stabilize As-rich	
	Emphasis on stabilization/ solidification (S/S)	Treating As containing wastes in water	
	Soil flushing using aqueous solutions using surfactants and solvents Adsorption by using specific media,	Applied in the field, efficiency can vary from 0% to almost 100%	
Chemical	immobilization, modified coagulation along with filtration, precipitations, immobilizations, and complexation reactions	Economic but often displayed lower Efficiencies (<90%)	[70, 73–76
	Formation of stable phases, for example, insoluble FeAsO ₄ (and hydrous species of this compound such as scorodite, FeAsO ₄ .2H ₂ O)	Use of selective stabilizing amendments is a challenging task	
	Stabilization method using nanosized oxides and Fe(0) (particle size of 1 to 100 nm)	Gained popularity/ high success rate, but it could be expensive when remediating a large area	
Intrinsic bioremediation	Degradation of arsenic by naturally occurring microorganism	More suitable for remediation of soil with a low level of contaminants	[77]
Engineered bioremediation	Optimizing the environment condition to promote the proliferation and activity of microorganisms	Favorable method used in high contaminated area	[78]

Method	Method in detail	Characteristics	Ref. [79]	
Microbial oxidation	Immobilization of As in the solid phase	Required biological activity, and microbiological molecular analysis/ involved adsorption or co-precipitation with Fe-ox hydroxides		
Physiochemical	Filtration or coagulation sedimentation, osmosis or electro dialysis, adsorptions, and chemical precipitations	Widely accepted in some places	[70, 73–76]	
		Widely accepted in some places	[70, 73–76]	
Phytoremediation	remediation Using "free-floating plants such as Widely a water hyacinth" Using aquatic rooted places plants such as Agrostis sp., <i>Pteris vittata</i> , and <i>Pteris cretica</i>		[70, 73–76]	
As(III) S-adenosylmethionine process of a		Is a reliable biological process of removing arsenic from aquatic mediums	[70]	
Reduction	Reduction of arsenate into arsenite by microorganisms via dissimilatory reduction mechanism	Should be carried out in facultative anaerobe or strict anaerobe condition	[70]	
Oxidation Using heterotrophic bacteria and chemoautotrophic bacteria to oxidize arsenite into a less toxic arsenate		Should be carried out in controlled environment	[80–83]	

Table 4.Characteristics of various methods for the removal of arsenic from aqueous system.

species separation, simple and cost-effective electrochemical methods were developed recently based on the distinct As-species electrochemical properties [84].

6. Conclusion

This chapter on removal of arsenic - "a silent killer" in the environment by adsorption methods has been discussed. Moreover, recently the consumers have become very much conscious about the environment, renaissance of eco-friendly products and process, which has thus become also important now. Thus, revival of natural arsenic application on various areas and summary of earlier researches on standardization of its method of extraction, mordanting, process variables and even natural finishing, etc. have been elaborated in this chapter. Thus this part has become a unique comprehensive chapter for information on removal of 'arsenic' a silent killer in the environment by adsorption method. A brief review of the removal of arsenic ions from water using iron-based adsorbents has been presented. A few adsorbents discussed in this chapter include relative advantages and disadvantages of adsorbents used for the removal of arsenic from water have been mentioned. The mechanism of arsenic adsorption on iron-containing adsorbents was summarized. Overall, there exist significant progress and benefit on using adsorption process for removing arsenic species from groundwater in a practical way to make potable water accessible for the rural population.

Conflict of interest

There is no conflict of interest.





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