



## Arsenic Mitigation by Natural Resources

Ashok Kumar Jha<sup>1\*</sup>, Sourav Majumder<sup>2</sup> and Yogesh Chandra Gupta<sup>3</sup>

<sup>1</sup>University Department of Chemistry, T.M.B.U, Bhagalpur, India

<sup>2</sup>Department of Chemistry, Kaliachak College, University of Gour Banga, Malda, India

<sup>3</sup>Department of Chemistry, M.S. College Alauli, India

\*Corresponding Author: Ashok Kumar Jha, University Department of Chemistry, T.M.B.U, Bhagalpur, India.

Received: October 31, 2020

Published: November 21, 2020

© All rights are reserved by Ashok Kumar Jha., et al.

### Abstract

This paper deals with the eco-friendly and low cost recent techniques of removal of arsenic from aqueous medium keeping in mind the health hazards of arsenic contamination.

Arsenic contamination in ground water of the Gangetic plain in Holocene newer alluvial due to arsenic bearing chemicals has become a matter of grave concern. As a result researches on arsenic mitigation using natural resources are going on in different parts of the world. Natural resources e.g. bentonite mineral of Rajmahal hills and aquatic plants have been utilized for removal of arsenic from aqueous medium. Aquatic plants remove arsenic through their roots and leaves known as phytoremediation and dried biomass is also useful for removal of arsenic known as bio-remediation. The presence of unsaturated carboxylic acid, hemicellulose and amino groups present on the surface of the biomass bind arsenic on the surface but bentonite mineral removes arsenic by adsorption and ion exchange both due to the presence of unsatisfied charges on the surface. Percentage removal of arsenic with varying time by bentonites and aquatic plants have been calculated and experimental data have been used to explain the nature of adsorption.

**Keywords:** Bentonite; Bio-remediation; Phytoremediation; Arsenic; Aquatic Plants

### Introduction

Ground water arsenic contamination has been reported in different parts of the world including Jharkhand, Bihar and Uttar Pradesh. The upper permissible limit of arsenic in drinking water is 0.05 ppm as per WHO guideline. The wide distribution of arsenic in the Gangetic plain has resulted in hyper pigmentation among the inhabitants of arsenic affected region [1-4]. Prolonged use of arsenic contaminated water may even lead to skin cancer [5]. Tube wells in Holocene Newer Alluvium are characterized by grey to black colored organic rich argillaceous sediments which

have arsenic contaminated ground water [6]. Main causes of occurrence of arsenic in ground water may be attributed to pyrite bearing shale, As- Cu mineralization and Gold belt of the Son valley with arsenic content. Arsenic problem is not only local and national but also global. The danger of arsenic contaminating water reserves in the entire world is on the rise. Most water enters from natural deposits in the earth. Arsenic occurs as arsenic sulphide minerals like arseno pyrites. Some of arsenic impurities exist in calcium carbonate and phosphate minerals where it substitutes for carbonate and phosphate. It has the property of exchange onto clay minerals.

In oxidizing soils arsenate is bound to ferric hydroxide minerals such as ferrihydrite and hematite. Organic matter converts ferric to more soluble ferrous, in effect dissolving arsenic and causing increase in arsenic in ground level. Use of arsenical pesticides, herbicides, industrial and agriculture pollution increases the arsenic level in ground water. Inorganic arsenicals are more toxic than organic arsenicals. As (III) is more toxic than As (V). An alarming aspect of arsenic contaminated groundwater is in its use of irrigating crops and vegetables to which arsenic passes and then consumed by humans.

The majority of arsenic present in the ground water is in the form of As (III) which exists as uncharged species arsenic tri hydroxide at pH value less than 9.2. As (III) is oxidized to As (V) by various techniques like coagulation micro filtration, fixed bed adsorption, lime softening, Ion exchange, Membrane filtration etc. Bentonites containing unit of montmorillonites have the capacity to remove arsenic from aqueous medium. On treatment of 100 ml arsenite solution with 300 mesh sieves bentonites up to different intervals of time, it has been found that bentonites are good adsorbent of arsenite. The adsorption isotherm and kinetic studies show that adsorption follows first order kinetics. A Freundlich isotherm is obeyed in the adsorption of arsenic by bentonite minerals. Adsorption of arsenic by bentonite minerals has proved to be a low cost ecofriendly method. Inorganic arsenicals are more toxic than organic arsenicals. Arsenic a metalloid, exists in three common oxidation states 0, +3 and +5. As (III) is more toxic than As (V) [7]. Arsenite exists in aqueous medium as  $H_2AsO_3$  and  $H_3AsO_3$  whereas arsenate is as  $HAsO_4^{2-}$  and  $H_2AsO_4^{2-}$ . Several aquatic weeds are available in abundance in the Gangetic plain which has been found as hyper accumulator of arsenic. *Typha latifolia*, *Lemna minor*, *Azolla* and *Eicchornea crassipes* are some of the plants which have been tested for arsenic removal [8]. This promising technology for arsenic removal consists of removal of pollutants by growing selected plants. This method is cost effective because the roots, stems and leaves absorb and degrade the pollutants from soil and water. *P. vittata* has been identified as the first arsenic hyper accumulator. The vacuoles of *P. vittata* cells are efficient for uptake of arsenic from water. Different varieties of *P. vittata* are Cretan Brake, *Pityrogramma calomelanos*, *Pteris cretica*, *Pteris longifolia*, *Pteris umbrosa*, *Pteris cretica chilsi*, *Pteris cretica rowerii*, *Pteris cretica parkerii* *Aberdeen*, *Pteris biaurita*, *Pteris quadriaurita*, *Pteris multifida* and *Pteris oshimensis*. The mechanism of arsenate or arsenite uptake by

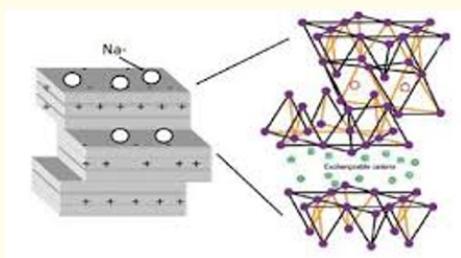
*P. vittata* is different [9]. *Cynodon dactylon* commonly found in most of the parts of the country has been found to be an effective phyto remediator of arsenic as hyper accumulator. Besides this, there are fern species which grow in a natural way in this region. Aquatic weeds have also the capacity to remove arsenic from aqueous medium. Some of the aquatic plants worth mentioning are *Hydrilla verticillata*, *Potamogeton pectinatus*, *Egeriadensa*, *Ceratophyllum demersum* and *Lepidium sativum* [10,11]. These aquatic plants accumulate arsenic through its root, stem and leave which may serve as an effective tool of removal of arsenic from aqueous medium [12,13].

*Azolla*, *Eicchornea crassipes* and *Lemna minor* are some of the common aquatic plants which can be seen in ponds and rivers of this region.

| S. No | Type                           | Classification sub merged hydrophytes | Effect                          |
|-------|--------------------------------|---------------------------------------|---------------------------------|
| 1     | <i>Hydrilla</i>                | Monocots                              | As, Cr, Cd                      |
| 2     | <i>Potamogeton</i>             | Monocots                              | Heavy metals                    |
| 3     | <i>Vellisneria</i>             | Monocots                              | Cr,NO <sub>3</sub> <sup>-</sup> |
| 4     | <i>Ceratophyllum</i>           | Dicots                                | Heavy metals                    |
| 5     | <i>Utricularia</i>             | Dicots                                | Heavy metals                    |
| 6     | <i>Spirallis</i>               | Dicots                                | Heavy metals                    |
| 7     | <i>Lemna</i>                   | Free floating hydrophytes             | As, Cr, Mn                      |
| 8     | <i>Spirodella</i>              | Free floating hydrophytes             | As, Cr, Mn                      |
| 9     | <i>Azolla</i>                  | Free floating hydrophytes             | As, Cr                          |
| 10    | <i>Eicchornea Crassipes</i>    | Free floating hydrophytes             | Cr, Cd                          |
| 11    | <i>Nymphaea (Water Lily)</i>   | Fixed floating hydrophyte             | As                              |
| 12    | <i>Nelumbium Jussiaea</i>      | Fixed floating hydrophyte             | Mn, Cr                          |
| 13    | <i>Victoria regia Marsilea</i> | Fixed floating hydrophyte             | Mn, Cr                          |
| 14    | <i>Thypha</i>                  | Amphibious                            | Cr, Mn                          |
| 15    | <i>Aquatilis</i>               | Amphibious                            | Mn, Cd                          |
| 16    | <i>Ipomea aquatica</i>         | Amphibious                            | Pb, Cd                          |
| 17    | <i>Sagittaria Alisma</i>       | Amphibious                            | Mn                              |

**Table 1:** Aquatic plants of Gangetic plain for Arsenic removal.

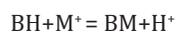
In view of above, aquatic weeds may be used as a safe route of accumulation of arsenic from water and soil. Thus, the detoxification by the use of aquatic plants needs to be stressed in order to make water and soil free from arsenic as well as heavy metals. Bentonites in different colors and grades are available in many states of the country. Rajmahal hill bentonites have been found as good quality bentonites due to its cation exchange capacity, swelling power and potential for adsorption. The bentonites minerals contain montmorillonite unit with very few impurities. The bentonites have been collected from Motijharna, Bakudih and sahibganj district of Jharkhand.



**Figure 1:** Structure of bentonite.

The lattice has negative charge which is balanced by the cations held on the surface. Grim in 1953 proposed the structure of Bentonite as 2:1 which implies that one octahedral sheet is sandwiched between two tetrahedral sheets. The exchangeable cations are  $\text{Na}^+$ ,  $\text{Ca}^{+2}$  and  $\text{Mg}^{+2}$  and the bentonites have a cation exchange capacity varying from 70 to 110 m eq/100 gm of clay.

The cation exchange capacity may be represented as



$\text{M}^+$  represents cation,  $\text{H}^+$  is cation.  $\text{M}^+$  exchanges  $\text{H}^+$  cation and  $\text{BH}$  is an exchanger.

$K = \frac{[\text{BM}][\text{H}^+]}{[\text{BH}][\text{M}^+]}$ , where  $K$  is thermodynamic equilibrium constant.

The molecular formula of Bentonite is  $(\text{Na}, \text{Ca})_{0.33} (\text{Al}, \text{Mg})_2 \text{Si}_4 \text{O}_{10} (\text{OH})_2 \cdot n \text{H}_2\text{O}$ . The main constituent of this Smectite clay mineral is Silica and Alumina. In addition to this Calcium oxide, Sodium oxide, Magnesium oxide, Ferrous oxide/Ferric oxide and traces of

Titanium oxide are present. Arsenic removal of water or prepared synthetic samples takes place both by ion exchange [14-16] and the surface area of bentonites available for adsorption. This is the explanation commonly offered by research workers on arsenic. The pure sample as well as derivatives of the collected bentonites from different places of Hazaribagh has also been analyzed for arsenic removal capacity [17,18]. These properties of bentonites have made them useful in drilling of oil wells, refining of oil and decoloration of wine [19].

The relative proportion of a sample is thus known because each element have different peak on its X-ray spectrum. The montmorillonites are represented by XRD patterns. Inter planar distance ( $\text{\AA}$ ) and corresponding relative intensities in 4.414, 4.3534, 4.396, 4.1984 ( $\text{\AA}$ ) having relative intensities 19.63, 90, 17.40, 17.55 respectively. In the OH- stretching region bands around 3620 to 3698  $\text{cm}^{-1}$  represent surface OHs and inner OH. Thus, the absorption bands at 3446 - 3698  $\text{cm}^{-1}$  represents fundamental stretching vibrations of different OH group e.g. Mg-OH-Al and Fe-OH-Al in the octahedral layer. The bands at 3698.03 and 3621.23 correspond to Al-OH vibration which characterizes montmorillonite. The higher bands are due to surface OHs and band at 3621.23 originates from the inner OH. A band at 3436  $\text{cm}^{-1}$  observed, indicates the presence of natural disordered Kaolinite in small proportion. 362  $\text{cm}^{-1}$  vibration indicates Al-OH-Al. The bands around at 778.2  $\text{cm}^{-1}$ , 995.60  $\text{cm}^{-1}$ , indicate the presence of MgO and  $\text{Al}_2\text{O}_3$  respectively. The peak at 1636. 10 shows the absorbed water between the layers. The peaks obtained in FTIR analysis characterize the vibration bands of montmorillonite. It may be concluded that peaks are identical to Na-montmorillonite derivative having trace of impurities e.g. Kaolinite. The effect of contact time with fixed mass of montmorillonite in 100 ml solution of sodium fluoride has been studied. TGA and DSC studies show a weight loss of 18.9% between 296 and 1173 k which is in agreement with the Wyoming bentonite [19]. This shows and confirms the presence of montmorillonite unit. Further FTIR shows the absorbate peaks of group present in the clay and PXRD analysis explains the diffraction pattern of the crystal [20]. Bentonites of Rajmahal hills have been found to be a potential remover of fluoride, heavy metals and arsenic too [21,22]. The adsorption mechanism has been explained by Freundlich Adsorption Isotherm, given as

$q_c = K.C^{1/n}$  or  $x/m = K.C^{1/n}$ , where  $x/m$  is the mass of adsorbate per unit adsorbent

$\log x/m = \log K + 1/n \log C$ , the value of  $K$  and  $1/n$  are obtained from the intercept and slope respectively.

The value of  $x/m$  or  $q_c$  is obtained from the formula given below

$$q_c = [(C_0 - C_e) \times V] / w$$

Where  $C_0$  and  $C_e$  are the initial and equilibrium concentrations of fluoride respectively.  $W$  is the mass of adsorbent and  $V$ , the volume of solution being used. The percentage removal is given by % removal =  $[(C_0 - C_t) / C_0] \times 100$  [23,24]. Percentage removal varies with time and maximum % removal is up to 90%.

The kinetics of adsorption is studied by the formulae  $K = 2.303 \log C_0 / C_t$ .

$C_0$  represents the initial concentration and  $C_t$  concentration at time  $t$ .

### Methodology

TGA analysis has been done to characterize the bentonite mineral in which a weight loss of 18.9% is observed. FTIR has been done to see the peaks in the spectrum which confirms the presence of different oxides described above. Intensities of the peaks in the PXRD analysis give diffraction pattern. All these tests characterize the bentonite mineral. After sample collection from different places bentonite is powdered to 300 mesh sieve and treated with 100 ml 2 ppm As (III) solution up to different intervals of time e.g. 1 hour, 2 hour, 3 hour. Percentage removal is up to 90%. Fixed weight of aquatic plants is treated with 100 ml 2 ppm As (III) solution up to different time intervals and percentage removal has been calculated [25,26]. Similar experiment has been repeated with dead biomass of leaves and stems [27,28]. Kinetics has also been studied.

### Conclusion

From different Government reports and tests performed, it is obvious that there is a rapid expansion of arsenic concentration in ground water in selected region which is a matter of great concern for the inhabitant of that region. Bentonites, their derivatives along with aquatic plants have emerged as a potential eco-friendly

and low cost remover of arsenic from water. Both Freundlich and Langmuir adsorption isotherms are followed in case of removal of arsenite by bentonites [29,30]. Removal of arsenic by bentonites and aquatic plants follow first order kinetics. Thus, these natural resources may be adopted as an alternative for arsenic removal.

### Bibliography

1. Kumari K and Jha AK. "Studies on concentration of Arsenic (III) and chromium (VI) in ground water resources of Naugachia region". *Journal of Emerging Technologies and Innovative Research* 6.2 (2019).
2. Jha AK and Gupta Y.C. "A case study of arsenic in koshi region of Khagaria district". *Chemical Science Review Letters* 6.24 (2017).
3. Jha AK and Kumar U. "A case study of arsenic and fluoride contamination in Bhagalpur district". *Journal of Chemical and Pharmaceutical Research* 6.2 (2014): 735-738.
4. Kumari Kiran and Jha Ashok Kumar. "Ground water: Physico-chemical assessment along the Koshi River in Kharik block of Naugachia subdivision, Bhagalpur". *Journal of Phamacognosy and phytochemistry* 8.3 (2019).
5. Jha AK and Kumar Ujjwal. "Estimation of arsenic (III) and Chromium (VI) contamination in Gangetic plains of Bhagalpur". *International Journal of New innovations in Engineering and Technology* 12.4 (2020).
6. Jha AK. "A Case study of water pollution of Kharnai river as well as ground water with special reference to heavy metals". *Indian Journal of Environment Protection* 10.30 (2010).
7. Jha AK. "Adsorption of Cr (VI) and Arsenic on to bentonite". *Chemical Science Review and Letters* 3.12 (2014).
8. Jha AK and U Kumar. "Studies on removal of heavy metals by Cymbopogon flexuosus". *AJAEB* 10.1 (2016): 89-92.
9. Xie En- Qing, et al. "The arsenic hyper accumulator fern pteris vittata L". *Environmental Science and Technology* 43.22 (2009).
10. Kumar Smita, et al. "Omics and biotechnology of arsenic stress and detoxification in plants: Current updates and prospective". *Environmental International* 74 (2015): 221-230.

11. Srivastava M., et al. "Effects of selenium on arsenic uptake in arsenic hyper accumulator P. Vittata L.,". *Bioresource Technology* 100 (2009): 1115-1121.
12. Zhao F., et al. "Arsenic uptake and metabolism in plants". *New Phytology* 181 (2009): 777-784.
13. Mehrag AA., et al. "Arsenic uptake and metabolism in arsenic resistant and non resistant species". *New Phytology* 154 (2002).
14. Majumder S and Jha Ashok Kumar. "Removal of Cr and Mn from aqueous medium using bentonites and their derivatives". *Journal of Chemical Science* 6.10 (2020).
15. Mishra B and Jha Ashok Kumar. "Chemical Composition and Molecular Formula of Rajmahal Bentonite (Jharkhand)". *Asian Journal of Chemistry* 23.12 (2011): 5491-5494.
16. Jha Ashok Kumar., et al. "Softening of hard water by bentonite mineral". *Asian Journal of Water, Environment and Pollution* 8.4 (2011).
17. Jha AK. "Bentonite for chemical industries". *Journal of Indian Chemical Society* 95.1 (2018).
18. Jha AK., et al. "Characterization of Montmorillonite minerals". *Journal of Emerging Technologies and Innovative Research* 6 (2019).
19. Jha AK. "Bentonite minerals and its TGA,DSC and PXRD studies". *Journal of Indian Chemical Society* 93 (2016): 437-442.
20. Jha AK and Mishra B. "Removal of fluoride by bentonite minerals of Rajmahal Hills". *Journal of Indian Chemical Society* 89 (2012): 519-521.
21. Singh B and Jha AK. "Defluoridation of water by montmorillonite minerals". *International Journal of Latest Transactions in Engineering and Science* 8.4 (2020).
22. Kumari Anjana., et al. "Adsorptive removal of chromium using rice husk and maize stem powder". *International Journal of Latest Transactions in Engineering and science* 8.4 (2020).
23. Kumar P Rohini., et al. "Utilization of Erythrina variegata orientali's leaf powder for the removal of cadmium". *Indian Journal of chemical Technology* 16.4 (2009): 308-316.
24. Riaz Muhammad., et al. "Pb (II) biosorption from hazardous aqueous streams using Gossypium hirsutum (cotton) waste biomass". *Journal of Hazardous Materials* 161 (2009): 88-94.
25. Mondal P., et al. "Treatment of arsenic contaminated water in laboratory scale up-flow bio-column reactor". *Journal of Hazardous Materials* 153 (2008): 136-143.
26. Biswas Biplob Kumar., et al. "Adsorptive removal of As (V) and As (III) from water by a Zr (IV)-loaded orange waste gel". *Journal of Hazardous Materials* 154 (2008): 1066-1074.
27. Ghimire K.N., et al. "Adsorptive removal of arsenic using orange Juice residue". *Separation Science and Technology* 37. (2002).
28. Saxena Renu and Sharma Sapna. "Isothermal study on removal of methyl red from aqueous solution using Aloe vera leaves powder". *Asian Journal of Chemistry* 29.12 (2007): 2743-2749.
29. Chatterjee Rajat and Majumder Chanchal. "Modelling of adsorption process in Industrial waste water treatment- A review". *Journal of the Indian Chemical Society* 96.4 (2019): 499-506.
30. Das Dimitra., et al. "Magnesium incorporated graphitic carbon nitride for effective removal of fluoride ions". *Journal of Indian Chemical Society* 96 (2019): 455-460.

#### Assets from publication with us

- Prompt Acknowledgement after receiving the article
- Thorough Double blinded peer review
- Rapid Publication
- Issue of Publication Certificate
- High visibility of your Published work

**Website:** [www.actascientific.com/](http://www.actascientific.com/)

**Submit Article:** [www.actascientific.com/submission.php](http://www.actascientific.com/submission.php)

**Email us:** [editor@actascientific.com](mailto:editor@actascientific.com)

**Contact us:** +91 9182824667