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Review Article

Arsenic Mitigation by Natural Resources

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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.

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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 been seen in ponds and rivers of this region.

S. No	Type	Classification sub merged hydrophytes	Effect
1	*Hydrilla*	Monocots	As, Cr, Cd
2	*Potamogeton*	Monocots	Heavy metals
3	*Vellisneria*	Monocots	Cr, NO_3^-
4	*Certophyllum*	Dicots	Heavy metals
5	*Utricularia*	Dicots	Heavy metals
6	*Spirallis*	Dicots	Heavy metals
7	*Lemna*	Free floating hydrophytes	As, Cr, Mn
8	*Spirodella*	Free floating hydrophytes	As, Cr, Mn
9	*Azolla*	Free floating hydrophytes	As, Cr
10	*Eicchornea Crassipes*	Free floating hydrophytes	Cr, Cd
11	*Nymphea (Water Lily)*	Fixed floating hydrophyte	As
12	*Nelumbium Jussiaea*	Fixed floating hydrophyte	Mn, Cr
13	*Victoria regia Marsilea*	Fixed floating hydrophyte	Mn, Cr
14	*Thypa*	Amphibious	Cr, Mn
15	*Aquatilis*	Amphibious	Mn, Cd
16	*Ipomea aquatica*	Amphibious	Pb, Cd
17	*Sagittaria Alisma*	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.

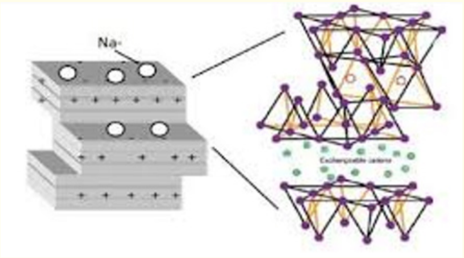

Figure 1: Structure of bentonite.

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 Na^{+1}, Ca^{+2} and 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

$BH+M^+ = BM+H^+$

M^+ represents cation, H^+ is cation. M^+ exchanges H^+ cation and BH is an exchanger.

$K= [BM][H^+]/[BH][M^+]$, where K is thermodynamic equilibrium constant.

The molecular formula of Bentonite is $(Na, Ca)_{0.33}$, $(Al, Mg)_2$, $Si_4O_{10}(OH)_2$. n H_2O. 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 decolouration 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 (Å) and corresponding relative intensities in 4.414, 4.3534, 4.396, 4.1984 (Å) having relative intensities 19.63, 90, 17.40, 17.55 respectively. In the OH- stretching region bands around 3620 to 3698 cm-^{1} represent surface OHs and inner OH. Thus, the absorption bands at 3446 - 3698 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 cm^{-1} observed, indicates the presence of natural disordered Kaolinite in small proportion .362 cm-^{1} vibration indicates Al-OH-Al. The bands around at 778.2 cm-^{1}, 995.60 cm-^{1}, indicate the presence of MgO and Al_2O_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

$q_c = [(C_0\text{-Ce}) \times V]/w$

Where C_0 and Ce 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 = $[(C_0\text{-Ct})/C_0] \times 100$ [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 $\log C_o \backslash_{C\,t}$.

Co represents the initial concentration and Ct 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. F.T.I.R 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.

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