Technique for arsenic removal from groundwater utilizing geological options—an innovative low cost remediation

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Abstract High arsenic levels in groundwater have emerged as a nagging problem in recent decades in different parts of the world. The high arsenic groundwater of the Holocene aquifers of the alluvial terrain of the Bengal Delta Plain (BDP) is unique and elusive in the extent of its exposure causing a threat to the lives of more than 70 million people. The present paper deals with the utilization of the indigenous geological material, laterite (or red earth) for removing arsenic from groundwater and potable water supplies. The aim is to devise a low cost arsenic filter unit using laterite. The material has been manipulated in several ways to study its applicability as an effective arsenic adsorbent. The results exhibit a removal efficiency of >90% and therefore can be implemented as an effective arsenic filter unit. Cost analysis shows that production of 10 l of water containing arsenic concentration as per WHO guidelines will cost US$ 0.625.

Key words arsenic; arsenic adsorbent; cost effective; laterite; technical feasibility

INTRODUCTION

High arsenic groundwater has lethal impacts on human health after prolonged consumption and is therefore a grim environmental problem. Cases of arsenic toxicity has been reported from several parts of the world, viz. Argentina, China, Taiwan, Thailand, Mexico, USA, Ghana, Hungary, UK, Chile, New Zealand and Russia. However, the vast Holocene alluvial aquifers of the Bengal Delta Plain (BDP) (lat. 21°30'N–27°10'N; long. 86°E–90°E) (Bhattacharya et al., 1997) comprising parts of West Bengal, India and Bangladesh, is demarcated as the worst affected area in the context of arsenic poisoning in groundwater (ACIC, 1998). The alluvial tracts of eight districts (Malda, Murshidabad, Nadia, Burdwan, Howrah, Hooghly, North and South 24 Parganas) of West Bengal, India are affected with high arsenic groundwater causing the health of more than thirty million people to be at risk (Mandal et al. 1996; Bhattacharya et al., 1997, 1998). Manifestations of arsenical dermatosis, hyperkeratosis, cirrhosis, portal fibrosis, pigmentation of palms and soles, melanosis and skin cancer (Chakraborty et al., 1987) are reported among the affected rural population.
Groundwater resources have been used exhaustively in the region over the last three decades to meet the need for sufficient drinking water supply for the ever-expanding population in a region with poor infrastructural facilities, as well as the green revolution. The uncontrolled and uncoordinated development of groundwater exacerbates the effects of the elevated level of arsenic in groundwater.

PROBABLE HYPOTHESES

Two hypotheses have been proposed to explain the origin and occurrence of dissolved high arsenic concentration in the groundwater: (a) the arsenic derives from the oxidation of pyrites/arsenopyrites in the aquifers as a result of over extraction of groundwater for irrigation for high delta paddy cultivation as well as to meet the drinking water crisis of over population (Das et al., 1996) and consequent aquifer dewatering; (b) the desorption of ferric hydroxide minerals present as coatings in the aquifer sediments under reducing groundwater conditions results in the co-dissolution of arsenic from sediment to groundwater.

The anaerobic conditions of the affected sedimentary aquifers can be visualized by the moderately low Eh data, low to very low dissolved oxygen content, and high dissolved iron (Fe(II)) concentration in groundwater (RGNDWM, 2000; Bhattacharya et al., 1997; Nickson et al., 1998, 2000). The low nitrate and sulphate content as well as presence of total organic carbon may perhaps facilitate the above process (RGNDWM, 2000). Research work carried out so far reveals that the reductive dissolution of ferric hydroxide is predominant in the sedimentary aquifers mobilizing arsenic in groundwater normally with soluble iron, Fe(II), phases.

ALTERNATIVES FOR SAFE DRINKING WATER SUPPLY

Several remedial options adopted, as well as implemented, in the action plans for the supply of potable water, did not yield promising results in the long run.

The adsorption–desorption phenomenon of arsenic in the natural environment is greatly influenced by the insoluble Fe(III)–soluble Fe(II) phase. Therefore, social acceptability, technical feasibility and economy of the remedial option(s) need to be critically scrutinized prior to the implementation for the long-term action plan of community water supply scheme in the rural and semi urban areas.

LOW COST REMEDIATION OPTION

The present contribution deals with a study on the use of geological material, laterite—the red earth (Fitzpatrick et al., 1983). Laterite (later = brick) (Buchanan et al., 1807) is a kind of indurated vesicular rock with highly ferruginous Fe(III) deposits and full of pores and cavities. Plausible reactions for adsorption of an anion on laterite are:

\[
\text{SOH}(s) + H^+(aq) = \text{SOH}_2^+(s) \quad (1)
\]

\[
\text{SOH}_2^+(s) + A^{l-}(aq) = S\text{A}^{(l-1)}(s) + \text{H}_2\text{O}(l) \quad (2)
\]

where S refers to the soil adsorbent.
The pH\textsubscript{zpc} (point of zero charge) of laterite on the basis of acid-base titration is found to be 8.5. Identical amounts of 5 g unsized crushed laterite (Medinipur) samples were subjected to different strengths of HCl, HAc, as well as NaOH washings respectively and the pH of each washed variety was recorded. Identical portions of 100 ml of solutions containing an initial concentration of 250 µg l\textsuperscript{-1} As(V) were added to each of the modified laterite varieties and the samples are shaken for 24 h to attain equilibrium. Solutions were then filtered through 0.2 µm polycarbonate filter and the final arsenic concentration was measured in each case. The pH of groundwater in the BDP varies between 6.5 and 7.5. Therefore laterite can perform efficiently in adsorbing arsenic over a wide pH range.

GEOCHEMISTRY OF LATERITE

Laterite is a vesicular clayey residuum of intensive chemical weathering of a wide variety of rocks under strongly oxidizing and leaching conditions occurring typically in tropical regions. The predominance of iron generally gives the rock its typical red colour. The major components in laterite are iron, aluminium, silicon, manganese, nickel and titanium in the form of hydroxides and/or oxides. Ferruginous, bauxitic and nickel type varieties are the most commonly found types of laterites. Laterite is an acidic soil with a typical pH between 4 and 5. Both hydrous iron and aluminium oxide components in laterite have a pH\textsubscript{zpc} at 8.5–8.6 (Anderson \textit{et al.}, 1976; Kinniburgh \textit{et al.}, 1976). Hydrous Fe- and Al- oxyhydroxide components of laterite, are characterized by a high positive surface charge at a wide pH range and therefore act as an adsorbent for several anionic contaminants (Pierce & Moore, 1982). Both oxy anionic arsenate and arsenite species have a strong tendency to adsorption on the oxide surfaces of laterite at a wide range of pH (Pierce & Moore, 1982).

The log $k$ values for the adsorption of the different pentavalent arsenic ions as well as trivalent arsenic species are cited below:

\begin{align*}
\text{\( \text{FeOH}^0 + \text{AsO}_4^{3-} + 3\text{H}^+ = \text{FeH}_2\text{AsO}_4^0 + \text{H}_2\text{O} \quad \log k = 29.31 \pm 1.02 \quad (3) \)} \\
\text{\( \text{FeOH}^0 + \text{AsO}_4^{3-} + 2\text{H}^+ = \text{FeH}_2\text{AsO}_4^0 + \text{H}_2\text{O} \quad \log k = 23.51 \pm 0.18 \quad (4) \)} \\
\text{\( \text{FeOH}^0 + \text{AsO}_4^{3-} + \text{H}^+ = \text{FeAsO}_4^{2-} + \text{H}_2\text{O} \quad \log k = \neg \quad (5) \)} \\
\text{\( \text{FeOH}^0 + \text{AsO}_4^{3-} = \text{FeOH}_2\text{AsO}_4^3 \quad \log k = 13.57 \pm 0.06 \quad (6) \)} \\
\text{\( \text{FeOH}^0 + \text{AsO}_3^{3-} = \text{FeH}_2\text{AsO}_3^1 + \text{H}_2\text{O} \quad \log k = 5.41 \pm 0.15 \quad (7) \)}
\end{align*}

The surface species $\text{FeAsO}_4^{2-}$ probably has no impact on the surface complexation of laterite.

In the present study the ferruginous variety of laterite, popularly called the red earth, from Medinipur in West Bengal, were used for the batch experiments.

The results reveal that the finer grains (Fig. 1) have the greatest adsorption area; nevertheless the unsized variety also has effective adsorption sites revealing the material to be porous in nature. Moreover, though the acid treated variety exhibits the greatest surface area for adsorption (Fig. 1), the ordinary variety is an efficient arsenic adsorber too due to the porous nature of the material. The unsized soil variety can be therefore used for commercial purposes instead of the fine variety which is labour intensive to prepare. The effect of time on the adsorptive capacity of laterite is
presented in Fig. 2. The results reveal that the difference between the first 10 min and several hours thereafter does not significantly affect the capacity. The adsorption process is highly effective during the first few minutes.

Figure 3(a) and (b) reveals a good correlation between adsorbed arsenic and iron in the treated laterite both under stirred and unstirred conditions. The stirring effect probably resulted in a greater scope for contact between the soil-solution surface.

Groundwater samples of initial pH 7.02 and initial total arsenic concentration 111.1 μg l⁻¹, were manipulated with HCl and NaOH to the desired pH values of 1–12. Laterite was added to the solutions, stirred for 1 min and left for one hour. The results are shown in Fig. 4. This reveals that laterite acts efficiently in adsorbing arsenic over a wide range of pH. However, under strongly acidic conditions the soil itself gets dissolved thereby decreasing its efficiency. Under strong alkaline conditions the iron content of laterite itself gets precipitated and a sharp fall in adsorbing capacity occurs. Laterite adsorbs As(V) predominantly at pH 4–5 whereas As(III) is effectively adsorbed at neutral pH.

A reasonable fall in the adsorbing efficiency in the above experiment at pH 4–5 indicates that As(III) is predominant in the BDP groundwater. The results obtained from a simple earthenware pitcher containing laterite as the filter media reveal that in addition to the adsorption of arsenic, laterite also plays a significant role in decreasing the amount of dissolved iron. The MnO₂ as well as TiO₂ content of the laterite probably facilitate the oxidation of the dissolved iron and arsenic content of the groundwater. The results are tabulated in Table 1.
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Figure 3: Relationship between adsorbed arsenic and iron in treated laterite under unstirred (a), and stirred (b) conditions.

Figure 4: Groundwater arsenic adsorption on laterite as a function of pH.

Table 1: Experimental results of pilot scale study using an earthenware pitcher impregnated with fixed bed laterite media.

<table>
<thead>
<tr>
<th>Trial run</th>
<th>Initial [As] (mg L⁻¹)</th>
<th>% As removal</th>
<th>Initial [Fe] (mg L⁻¹)</th>
<th>% Fe removal</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.133</td>
<td>88</td>
<td>2.875</td>
<td>71</td>
</tr>
<tr>
<td>2</td>
<td>0.263</td>
<td>97</td>
<td>2.623</td>
<td>78</td>
</tr>
<tr>
<td>3</td>
<td>0.168</td>
<td>94</td>
<td>0.143</td>
<td>84</td>
</tr>
<tr>
<td>4</td>
<td>0.017</td>
<td>41</td>
<td>3.501</td>
<td>91</td>
</tr>
<tr>
<td>5</td>
<td>0.263</td>
<td>96</td>
<td>0.143</td>
<td>69</td>
</tr>
<tr>
<td>6</td>
<td>0.229</td>
<td>96</td>
<td>1.934</td>
<td>95</td>
</tr>
</tbody>
</table>

ECONOMIC ASPECTS

Laterite is an indigenous natural material abundantly available in India. The cost calculated for the transportation of laterite approximates to about US$1.5 per 10 kg
laterite per km. The treatment process is estimated to cost about US$0.625 to produce ten litres of water containing arsenic concentration as per WHO guidelines. Therefore fixed bed laterite can be successfully employed on a large scale for removal of arsenic from groundwater.

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REFERENCES


