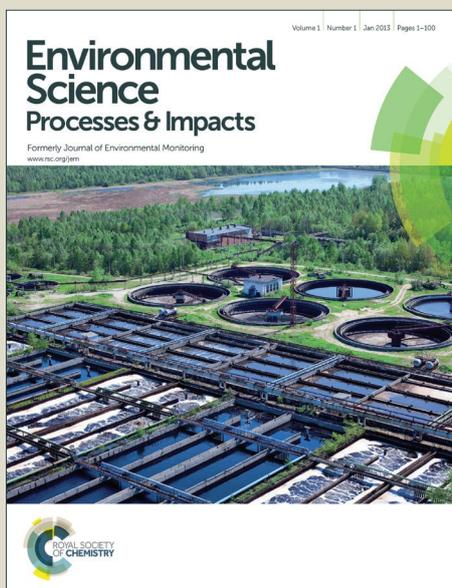


Environmental Science Processes & Impacts

Accepted Manuscript



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this *Accepted Manuscript* with the edited and formatted *Advance Article* as soon as it is available.

You can find more information about *Accepted Manuscripts* in the [Information for Authors](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the [Ethical guidelines](#) still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.



rsc.li/process-impacts

1
2
3 The paper addressed the natural attenuation capacities of the sediments commonly found
4 in the Brahmaputra Floodplains of Assam. A batch sorption experiment was conducted to
5 evaluate mechanism of sorption of arsenic from three different types of natural sediments
6 and the effects of co-anions in the adsorption capacities. Finally, oxidation of As(III) to
7 As(V) test suggested that oxidation to As(V) on oxidative site as main removal
8 mechanism in the oxidized sediments. This suggested that not only reduction in toxicity
9 but also immobilization is achieved, since As(V) having higher affinity for adsorption.
10 Therefore, the study helps in targeting safe aquifer (i.e. oxidized sediment) which could
11 naturally attenuate arsenic to lower level.
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60



Journal Name

ARTICLE

Natural attenuation processes of Arsenic in the groundwater of Brahmaputra floodplain of Assam, IndiaLalsangzela Sailo,^a and Chandan Mahanta^bReceived 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

Natural attenuation of higher arsenic (As) concentration in the groundwater of Brahmaputra valley of Assam, can be a viable options for its remediation. The assessment of attenuation capacities in the aquifers was done using three sediments core samples (namely C_50, C_70 and C_150) representing the commonly found sediments and characterized as viz. reduced, oxidized and moderately oxidized sediment respectively. The viability of aquifers to release low As water depends on the sorption capacity of the sediments to directly adsorbed as As(III) and/or oxidation to As(V) on oxidative sites. The various batch sorption experiments along with competition of other anions on adsorption at different concentrations were investigated. The sediments were observed to adsorbed both As(III) and As(V) with varying magnitude depending on the species of As, pH and concentrations of competing anions. Elovich kinetic model best described kinetic test data. The oxidized sediment (C_70) with highest Fe and Mn content has highest adsorption capacity. The competition of adsorption sites with As(V) in the sediment samples followed the order $\text{PO}_4^{3-} > \text{SiO}_2 > \text{HCO}_3^-$. The oxidation of As(III) to As(V) by the sediments was analyzed as it also most effective pathways to reduce the toxicity as well as mobility of As in the subsurface environment. Sediment C_70 showed highest potential to oxidized As(III) to As(V) in the oxidative sites of the sediments. The removal of As(III) in the oxidative site via As(V), was the dominant As removal mechanism for oxidized sediment (C_70) and moderately oxidized sediment (C_150) than direct adsorption of As(III) on the adsorptive sites as on reduced sediment sample C_50. Therefore, targeting oxidized sediment with high concentration of Fe-oxides and Mn-oxides might make natural attenuation of As viable in the study areas.

1. Introduction

Elevated concentrations of arsenic (As) in the shallow groundwater of Tokobari village, in Jorhat district of the Brahmaputra valley in the Northeastern part of India posed a potential As contaminated health risk. Since, the absence of main anthropogenic sources of As it was considered to be geogenic. The As contamination in the Assam floodplains of Brahmaputra River has been a serious concern due to the widespread dependence of the population on groundwater for drinking, domestic and irrigation purposes¹. The sources of As in the region may be primarily the sediments derived from the weathering and erosion of lithified crystalline rocks of Himalaya and adjacent regions of Bangladesh² which have similar hydrogeologic deposition³. These sediments were transported by the big river of Brahmaputra, deposited along

with organic matter, thus becoming sources of As to the groundwater^{4,5}. High As groundwater area are usually associated with reduced aquifers with high organic carbon and composed of gray to black sand⁶⁻¹⁰. The arsenite As(III) was found to be the dominant species than arsenate As(V) in reducing environment groundwater of the study¹¹.

Arsenic concentration in groundwater is usually controlled by natural geochemical processes, where adsorption-desorption reaction of As species on mineral plays a key role^{3,12,13}. The adsorption-desorption processes are also important for natural attenuation and water purification technologies, with the aim of removing As from water^{14,15}. The viability of aquifers to release low As water depends on the capacity of the sediments to remove As from the groundwater that could infiltrate from the zone of high organic content and strongly reduced sediments. Adsorption is one of the most commonly reported mechanism and possibly the initial reaction to occur when As interacts with sediments^{14,16,17}. Since, adsorption and oxidation of As regulates its fate and transport in the sediment, factors controlling the sorption process is of paramount importance. Numerous factors affect the efficiency of As adsorption, but adsorption study of As on sediments has been mainly linked to environmental factors such as pH¹⁸⁻²². The redox potential, reaction time^{16,23}, oxidation state of As^{16,17,20} and presence of

^a School of Engineering and Technology, Mizoram University, email: zelasailo@gmail.com

^b Dept. of Civil Engineering, Indian Institute of Technology Guwahati, email: mahantait@gmail.com

† Footnotes relating to the title and/or authors should appear here.
Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x

competing anions^{17,24-26}. The competition for sorption sites and various surface complexation models simulating the actual field condition has also been attempted^{7,21,22,27-30}. Color characterization of the aquifer for targeting safe arsenic drinking in shallow wells of Bengal basin have been already reported^{6,7,8}.

The oxidation of As(III) to As(V) by the sediment was studied as it not only decreased the toxicity of As, but helps immobilize it. There is evidence of oxidation of As(III) to As(V) by Mn-oxides, which also could be an important factor controlling the As species and the extent of As adsorption by the sediments^{17,31}. However, oxidation of As(III) by Fe(III) hydroxide in lake sediment has been reported previously³², possibly because of the high Fe(III):As(III) ratio. As(III) oxidation by MnO₂ was found to occur abiotically^{31,33}; however, several microbial respiratory and non-respiratory enzymatic systems for oxidation of As(III) have been reported³⁴.

In this study, we focused on examining As sorption as well as oxidation to As(V) processes in the selected three sediment samples which are commonly found in the area namely C_50, C_70 and C_150 (at a depth of 50ft, 70ft and 150ft), to gain an understanding for possible remediation and for delineating sources of low As groundwater. The characteristics of the sediment samples derived from SSE is shown (Table 1). The effects of pH, phosphate (PO₄³⁻), silica (Si) and bicarbonate (HCO₃⁻) and combined anions effects on As adsorption was evaluated using batch experiment. Finally, the oxidation of As(III) to As(V) test was performed to analyzed the sediments capacity to attenuate the As pollution and its mobility in the sub-surface environments.

2. Materials and Methods

2.1 Study Area

Samples of groundwater and sediment were collected from Titabor (Tokobari) area of Jorhat District in Assam, India. The study area is situated in the eastern part of Assam state of India between Latitude 26°27.3' North and 26°30.8' N, Longitude 94°6.3' E and 94°9.8' E (Fig 1). The site is located at an elevation slightly higher than the present day floodplains with younger alluvial deposits and Brahmaputra flows on the northern side of the district. The mean annual rainfall in the district is 2,197 mm. The sub-surface material consists of gravels, sands, silts and clays¹. The depth of hand tubewells are within 40m-50m depth. Old meanders, paleochannels (abandoned channels), natural levees, ox-bow lakes and water bodies are very common in the area¹. From the study area, 44 groundwater samples were collected during November 2008 to January 2010 from existing tubewells. The tubewell were classified as shallow tubewells as the depths were mostly between 40 to 50 m¹. Sediment sampling was simultaneously done.

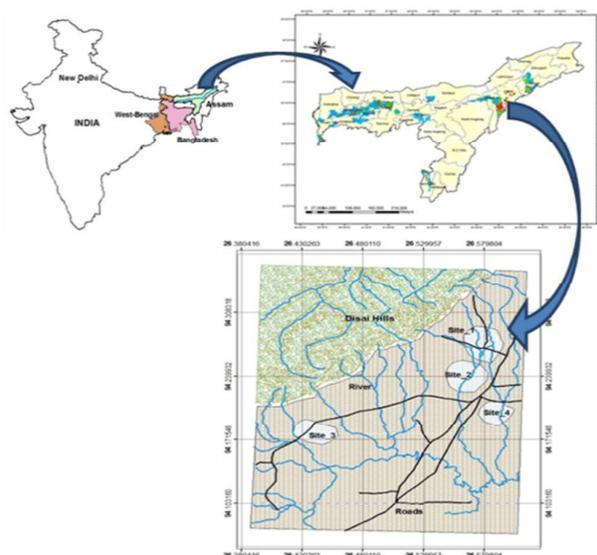


Fig. 1. Location of the study area Tokobari, Jorhat district.

2.2 Sample Collection

Based on the results of groundwater and sediment sample, six boreholes were drilled adjacent to two higher As contaminated tubewell (T1 and T2 >300µg/l as shown in Fig A1) in the latter part of January 2010 to understand the mobilization and immobilization processes governing in the sub-surface. During drilling, the color and texture of the sediment were noted and samples were collected in clean sealed airtight polyethylene bags and stored in dark until analysis was complete. The sediment samples were analysed for its physical, morphological and chemical properties³⁵.

2.3 Batch Experiment

The aim of batch sorption study was to examine the mechanism and extent of arsenic uptake in laboratory batch experiment using field sediments from cores taken at the 1C from the study site in order to quantify the ability of natural sediments to attenuate As present in groundwater. Three sediment samples C_50, C_70 and C_150 were chosen for batch experiment, and characteristics of these sediments were evaluated (Table 1). Reduced sediment (C_50) was characterized by gray color with low Fe and Mn, while oxidized sediment (C_70) was brown in colour with high concentration of Fe and Mn, while moderately oxidized sediment (C_150) had moderate value of Fe and Mn. Most tubewell screens were located at this depth (~ 46 m) i.e. C_150. These sediment samples analysed were present in most of the sediment core samples from the area, which may have different geochemical properties for the release of As into the groundwater.

Table 1. Characteristics of the sediment samples and results of selective sequential extraction (SSE).

| Sample ID | Color | Depth (m) | Reductively extracted Fe (mg/kg) | Reductively extracted Mn (mg/kg) |
|-----------|--------------|-----------|----------------------------------|----------------------------------|
| C_50 | Gray | 15 | 3000 | 8 |
| C_70 | Brown | 21 | 28000 | 200 |
| C_150 | Ash-Greenish | 46 | 7000 | 160 |

All the experiments were performed with synthetic, arsenic spiked groundwater with equivalent characteristics of groundwater of the study area as far as possible. The solutions contained Ca^{2+} 16 mg/l, Mg^{2+} 10 mg/l, K^+ 3 mg/l which was broadly comparable to the natural groundwater of the study area that was used in all the batch experiments¹¹. In preparing the solutions, chloride forms were used (Viz. CaCl_2 , MgCl_2 , KCl and NaCl) in these experiments to avoid adsorption effect from HCO_3^- salts and slightly higher of Cl^- concentration was observed. The molar concentration method of calculation was used to get the desired concentrations of cations to find the competition of anions onto sorption properties. The pH of the solution was set to 6.5 which was the mean pH of the groundwater samples. The stock solutions were prepared from reagent grade sources i.e. As(V) from $\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$, As(III) from NaAsO_2 , PO_4^{3-} from K_2HPO_4 , Si (silica) from $\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$ and HCO_3^- from NaHCO_3 .

2.3.1 Batch Sorption Kinetic Study

Arsenic removal kinetic tests for As(III) and As(V) by the sediment samples viz. C_50, C_70 and C_150 experiments were conducted using 50 ml polyethylene centrifuge tubes at room temperature (26 ± 2 °C) in 1:20 soil/water ratio. The two initial As concentrations chosen to replicates the groundwater were 300 $\mu\text{g/l}$ and 500 $\mu\text{g/l}$ for competition of ions. The samples were gently shaken in horizontal shaker at an rpm of 180 for 1440 minutes (24 hours). The tubes along with its duplicates were withdrawn at predefined time interval (i.e. 5, 10, 20, 30, 60, 120, 240, 360, 600, 1440 minutes) and then centrifuged at 9000 rpm for 15 minutes and supernatants were collected using a syringe. The amount of As adsorbed per unit mass of sediment ($\mu\text{g/g}$) was calculated from Eq. 1 and the sorption percentage using Eq. 2. The various adsorption model viz. pseudo-second order kinetic model, Elovich model and Intraparticle diffusion model were fitted for each of the As species.

The amount of As adsorbed per unit mass of sediment ($\mu\text{g/g}$) was calculated from the difference between the concentration of the supernatant and that of the initial solutions using following equation:

$$q_t = (C_i - C_e) \frac{V}{W} \quad (1)$$

where C_i and C_e are the arsenic concentration ($\mu\text{g/l}$) at initial and equilibrium respectively, V the volume of solution (ml), W

is the weight of sediment (mg). The amount of As adsorption (S%) was calculated as follows:

$$S\% = \frac{(C_o - C_f)}{C_o} \times 100 \quad (2)$$

where S is the As adsorption (%); C_o is the initial concentration of the As in sediment-less blank ($\mu\text{g/l}$); C_f is the final concentration of As ($\mu\text{g/l}$).

2.3.1.1 Elovich Kinetic Model

The Elovich equation has been widely used in adsorption kinetics, which described chemical adsorption in nature such as soils³⁶. The Elovich equation can be written in the form³⁷:

$$\frac{dq_t}{dt} = a \exp(-bq_t) \quad (3)$$

where a represents the rate of chemisorption at zero coverage ($\mu\text{g}/(\text{g min})$) and b is the extent of surface coverage and activation energy for chemisorptions ($\text{g}/\mu\text{g}$) i.e. b value is indicative of the number of sites available for adsorption. The application of Eq. (4) is usually tested by converting it to the integrated form, given that $q_t = 0$ at $t = 0$ and $q_t = q_t$ at $t = t$, where $t_o = 1/ab$. If $t \gg t_o$, the above Eq. (4) can be simplified as

$$q_t = \left(\frac{1}{b}\right) \ln(ab) - \left(\frac{1}{b}\right) \ln(t) \quad (4)$$

The constants a and b were calculated from the slope and intercept of plot q_t versus $\ln(t)$.

2.3.1.2 Intraparticle Diffusion Model

It is usually difficult to apply simple kinetics equations to describe sediment chemical reactions, since the sediment surfaces are heterogeneous and one cannot differentiate transport effect from chemical kinetics. The most-widely applied intraparticle diffusion equation was given by Weber and Morris (1963)³⁸:

$$q_t = K_i t^{0.5} + c \quad (5)$$

Where K_i is the intra-particle diffusion rate constant ($\mu\text{g}/(\text{mg min}^{0.5})$) and the intercept C is obtained by extrapolation of the linear portion of the plot of q_t versus $t^{0.5}$, back to the axis is taken to be proportional to the extent of the boundary layer thickness. The intra-particle diffusion plots show multi-linearity in the sorption process indicating the number of steps that are operational.

2.3.2 Batch Adsorption Study

Batch adsorption isotherm experiments were carried out under similar conditions explained for kinetic study. The study for the sorption isotherm was performed with different initial arsenic solution [As(V) and As(III)] of 100 $\mu\text{g/L}$, 200 $\mu\text{g/L}$, 300 $\mu\text{g/L}$, 400 $\mu\text{g/L}$, 500 $\mu\text{g/L}$, 700 $\mu\text{g/L}$ and 1000 $\mu\text{g/L}$ was used. Blank samples without As were also included in the experiment to verify the desorption of As from sediment. The effects of pH, competing anions viz. PO_4^{3-} , SiO_2 and HCO_3^- on the adsorption of As was studied and combined effect of the anions was evaluated.

Freundlich and Langmuir adsorption isotherms were fitted on the observed experimental data. The Langmuir equation can be written in the following linear form³⁹:

$$\frac{C_e}{q_e} = \frac{1}{q_{\max}C_e} + \frac{1}{K_L q_{\max}} \quad (6)$$

where q_e is the adsorption capacity at equilibrium (mg/g), q_{\max} is the theoretical maximum adsorption capacity of the adsorbent (mg/g), K_L is the Langmuir affinity constant (l/mg) and C_e is the supernatant equilibrium concentration of the system (mg/l).

In Freundlich adsorption model the adsorbed mass per mass of adsorbent can be expressed by a power law function of the solute concentration⁴⁰:

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \quad (7)$$

Where, q_e is the adsorption at equilibrium ($\mu\text{g/g}$), C_e being concentration ($\mu\text{g/l}$) at equilibrium, K_f and n represent the adsorption capacity and the adsorption intensity, respectively. The plot of $\log q_e$ versus $\log C_e$ has a slope with the value of $1/n$ and an intercept magnitude of $\log K_f$.

2.3.3 Validity of the Models

To get insight into the actual adsorption process, various adsorption kinetics models were fitted with the experimental data. The validity of various adsorption models were tested and quantitatively checked using coefficient of determination (r^2) between the actual experimental results and the model output. The coefficient of determination (r^2) to test the best-fitting of the kinetic model to the experimental data was calculated as

$$r^2 = \frac{\sum(q_m - \bar{q}_t)^2}{\sum(q_m - \bar{q}_t)^2 + \sum(q_m - q_t)^2} \quad (8)$$

Where q_m is the amount of As ion adsorbed on the surface of the sediment at any time, t , ($\mu\text{g/mg}$) obtained from the model, q_t is the amount of As ion on adsorbed on the surface of the sediment at any time t ($\mu\text{g/mg}$) obtained from experiment, and \bar{q}_t is the average of q_t ($\mu\text{g/mg}$).

2.4 Oxidation Kinetics of As(III) to As(V)

The oxidation kinetics of As(III) to As(V) experiments were carried out under similar condition with the sorption kinetics. The supernatant was collected from the tube by decantation after rotating in dark in horizontal shaker @ 180 rpm and the solid was used for the analysis of solid phase As. Then the solid-bound arsenic species were desorbed by adding 25 mL of 0.2M oxalic acid after the removal of the supernatant³¹. The tubes were then rotated in the dark for 15 min and centrifuged to remove the supernatant containing the desorbed arsenic species. The solid bound As was speciated to As(III) and As(V) to determine the adsorption and oxidation in the soil sediment samples.

Speciation of As species was performed with disposable cartridges (MetalSoft Centre). Speciation of the dissolved arsenic was determined by passing 50 mL of the supernatant

through the cartridges at a flow rate of 60 ± 30 ml per minutes using 50 ml syringe. Under our experimental conditions, As(V) is present predominantly as H_2AsO_4^- and is removed by the cartridge, whereas As(III) is present predominantly as H_3AsO_3 and elutes through the cartridge column.

Speciation of the solid phase As species was determined by adjusting the pH of the supernatant from the oxalic acid extract to approximately 4.5 by adding 10M NaOH. The As(III) concentration was determined from the eluting solution from the cartridge, and the As(V) concentration was determined by the difference between the total arsenic concentration in the supernatant and the As(III) concentration. Mass balance of arsenic species was achieved as a summation of solid-phase As(III) and As(V) concentrations and total aqueous As(III) concentration.

3. Results and Discussions

The sediments from the study areas contain a range of reactive functional groups that originate from the mixture of mineral phases and their surface coatings. The surface coatings were generally comprised of Fe, Al and Si, with lesser amounts of Mn as can be seen from the SEM/EDX, likely in the form of Fe(III) hydroxides, Al hydroxides and silicates, and Mn oxides (Appendix Figure A2 and A3).

3.1 Arsenic Adsorption Isotherm

From the batch experimental study, it was found that the sediments can adsorb As(III) and As(V), for the three sediment samples viz. C_50, C_70 and C_150 (Fig 2a-b). Freundlich and Langmuir adsorption isotherms were fitted into the experimental data (Table 2). It revealed that the highest As adsorption capacity was obtained for sediment sample C_70 which is consistent with the highest Fe and Mn content. The Fe-amorphous and Fe-crystalline oxides had high affinity for As sorption^{18,20,41,42}. Lower adsorption was observed for samples C_50 and C_150, and they had nearly comparable adsorption capacities. The adsorption of As(V) was found to be higher than As(III) and the adsorption behaviour of As(V) and As(III) onto Fe(III) oxides minerals is similar at pH 6.5 to 8²⁰. Since the pH of the groundwater was found to be near neutral condition, it was expected that the oxidized sediments would also have significant capacity to adsorb As(III) as shown (Fig 2a-b).

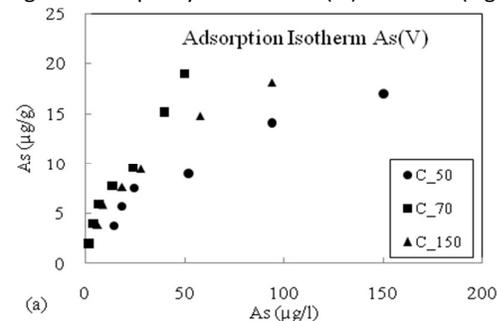


Fig. 2. (a) Adsorption isotherm for As(V), for the three sediment samples C_50, C_70 and C_150.

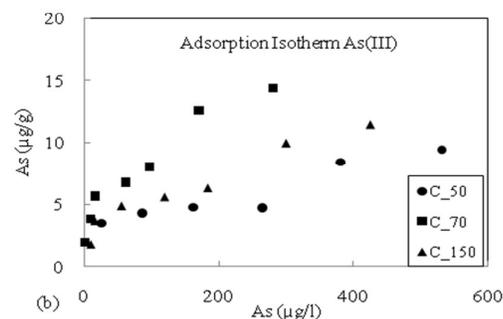


Fig. 2. (b) Adsorption isotherm for As(III) for the three sediment samples C_50, C_70 and C_150.

The quantification of As(III) was complicated by the fact that some of the As(III) was oxidized to As(V)^{17,31}. In the batch adsorption study of As(III), low concentration of aqueous As(V) was found. The experiment revealed that the oxidation might have taken place on the solid phase (sediment) oxidative sites and get adsorbed to the surface without releasing the As(V) into the solution.

Table 2. Freundlich and Langmuir adsorption isotherm parameters for sediments samples.

| As | Isotherm | parameters | C_50 | C_70 | C_150 |
|---------|------------|------------|------|-------|-------|
| As(III) | Freundlich | log K_f | 0.2 | 0.25 | -0.02 |
| | | 1/n | 0.24 | 0.36 | 0.42 |
| | | r^2 | 0.66 | 0.95 | 0.89 |
| As(V) | Freundlich | log K_f | 0.17 | 0.184 | 0.21 |
| | | 1/n | 0.47 | 0.626 | 0.52 |
| | | r^2 | 0.94 | 0.97 | 0.97 |
| As(III) | Langmuir | q_{max} | 7.7 | 15.6 | 12.5 |
| | | K_L | 0.01 | 0.02 | 0.01 |
| | | r^2 | 0.69 | 0.87 | 0.85 |
| As(V) | Langmuir | q_{max} | 21.7 | 26.3 | 22.2 |
| | | K_L | 0.02 | 0.03 | 0.03 |
| | | r^2 | 0.95 | 0.85 | 0.97 |

3.1.1 Effect of pH

The effect of pH on adsorption of As(III) and As(V) on the sediment samples have been studied at pH 6, 7.5, 8.5 (Fig 3a-b), which corresponds to natural groundwater condition. It was observed that with increase in pH to 8.5, the As(V) adsorption reduced by 10%, 4.5% and 5.5% for sediment samples C_50, C_70 and C_150. As(III) adsorption increased as pH increased, slight increase in adsorption were noticed viz. 6% for both C_50 and C_150 and 3.5% for C_70 sediment samples. The decrease in concentration of As(V) with increase in pH implies decrease in surface charged density due to increase of OH⁻ resulted in the electrostatic repulsion with oxyanions As(V) comparing with As(III) which has less negative character^{16,19,20}. Similarly, minimal effect of As(V) adsorption on Fe-oxides was noticed near neutral pH^{17,43}. May be due to

high Fe-oxides in the sediment samples and the point of zero charge (PZC) for Fe-oxides is in the pH range of 6-8⁴⁴, the adsorption of As(V) is preferred over As(III). The results further indicates that the pH has significant influence on the mobility of As(III) and As(V) in the aquifer. When the pH reduces the component of As(III) forms >Fe-wH₂AsO₃ and As(V) forms >Fe-wHAsO₄⁻ complexes and consequently the adsorption of As(III) and As(V) are constrained and favoured respectively²². The As(V) species Hfo_wHAsO₄⁻ has comparative lower formation constant there is depression in As sorption near neutral pH²¹. At the same time protonation of weak sites reduces the surface negative charge and thus reduces electrostatic repulsion during the adsorption of negatively charged oxyanions of As(V).

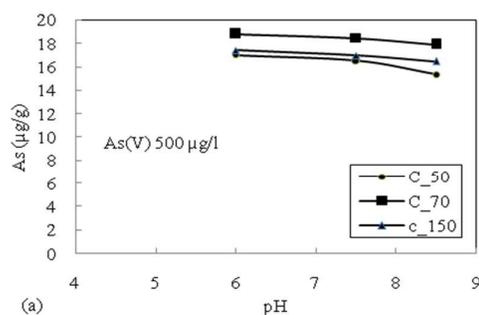


Fig. 3a. Effect of pH on adsorption of As(V) initial concentration of 500 µg/l for sediment samples

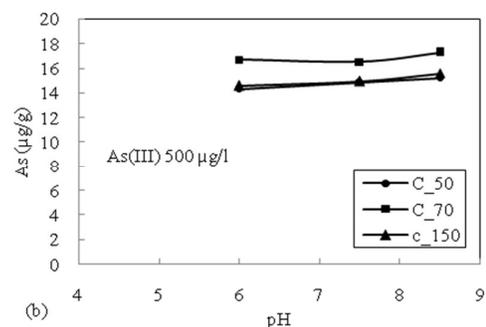


Fig. 3b. Effect of pH on adsorption of As(III) 500 µg/l for sediment samples.

3.1.2 Effect of Phosphate (PO₄³⁻)

In the batch experiment a strong competition for adsorption sites between As(V) and PO₄³⁻ was observed in the samples when the concentration of PO₄³⁻ was increased from 0.5 – 3 mg/l (Fig 4a-b). The decrease in As(V) adsorption depends on the ratio of PO₄³⁻/As(V) in the solution⁹. The competition for adsorption site by PO₄³⁻ was proposed to be main As releasing mechanism by few authors^{24,26,45,46}.

A highest reduction in the adsorption capacity was noticed in the reduced sediment sample C_50 (gray color sediment). The reduction in adsorption of As(V) with 500 µg/l initial concentration were 16%, 11% and 13% for C_50, C_70 and C_150 respectively and similar trend of was noticed for As(V)

concentration of 300 $\mu\text{g/l}$. The reduction of surface potential due to the formation of inner sphere complex with Fe-oxides also reduces the adsorption of As(V) due to electrostatic repulsion of similar charge on the sediment surface¹⁶. Therefore, the accumulation or precipitation of PO_4^{3-} on sediment might also promote the formation of negatively charged surface sites, which reduces the As(V) adsorption capacity.

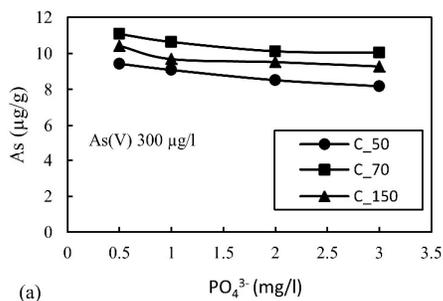


Fig. 4a. Effect of phosphate (PO_4^{3-}) on adsorption of As(V) with initial concentration of 300 $\mu\text{g/l}$

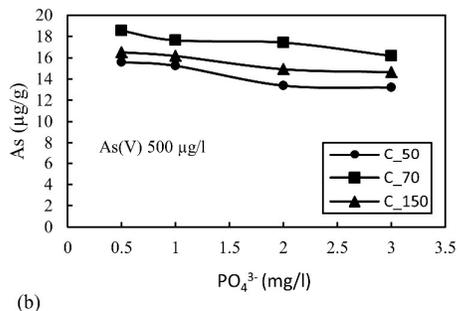


Fig. 4b. Effect of phosphate (PO_4^{3-}) on adsorption of As(V) with initial concentration of 500 $\mu\text{g/l}$ on sediment samples

3.1.3 Effect of Silica (SiO_2)

The competition of adsorption sites between As and silica (SiO_2) has been reported in Bangladesh²⁸. The effects of silica on the adsorption of As(V) was studied by varying the silica concentration viz. 10, 20, 30 mg/l. The experimental results (Fig 5a-b) shows that silica had lesser effect on As(V) adsorption on the sediment sample. The reduction in the As(V) adsorption when silica concentration increases from 10 to 30 mg/l for initial As(V) 500 $\mu\text{g/l}$ concentration were 10 % for both C_50 and C_150, 7% for C_70, and a decreasing adsorption was observed for initial As(V) concentration 300 $\mu\text{g/l}$.

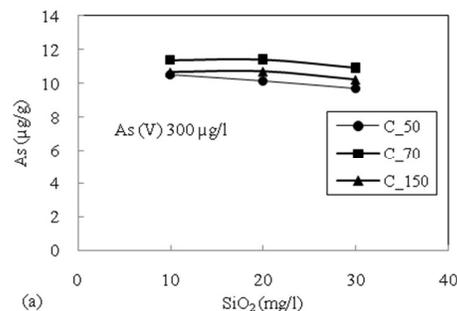


Fig. 5a. Effect of silica (SiO_2) on adsorption of As(V) with initial concentration of 300 $\mu\text{g/l}$

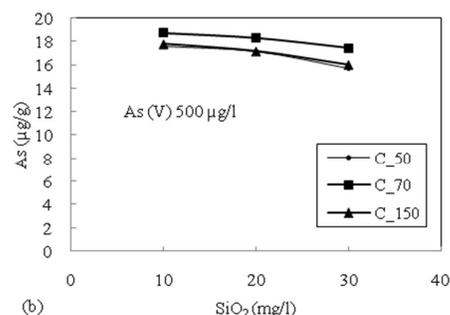


Fig. 5b. Effect of silica (SiO_2) on adsorption of As(V) with initial concentration of 500 $\mu\text{g/l}$ for sediment samples.

3.1.4 Effect of Bicarbonate (HCO_3^-)

Bicarbonate (HCO_3^-) is the most abundant constituent in groundwater from the study area. In the shallow aquifer of Bangladesh, high arsenic concentration was attributed to HCO_3^- ^{4,5,25,47}. The effects of HCO_3^- concentration in the groundwater for As(V) adsorption had been investigated by increasing the concentration of HCO_3^- from 200, 300, 400 and 500 mg/l. The results showed that bicarbonate has lesser pronounced effect on the adsorption than phosphate and silica. About 5% decrease in adsorption was observed in the sediment with increased in the bicarbonate concentration, for initial As(V) concentrations of 300 $\mu\text{g/l}$ and 500 $\mu\text{g/l}$ (Fig 6a-b).

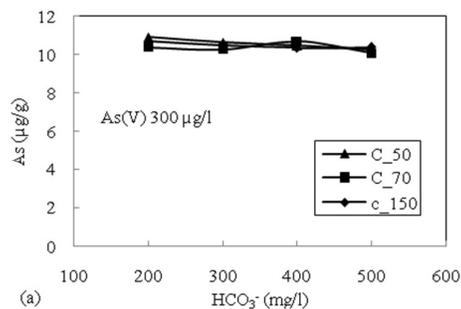


Fig. 6a. Effect of bicarbonate (HCO_3^-) on adsorption of As(V) with initial concentration of 300 $\mu\text{g/l}$ for sediment samples.

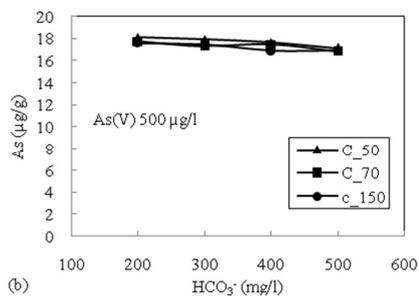


Fig. 6b. Effect of bicarbonate (HCO_3^-) on adsorption of As(V) with initial concentration of $500 \mu\text{g/l}$ for sediment samples.

3.1.5 Combined Anions Effect

The competitive nature of anions present in the groundwater was tested using a solution that could closely simulate the actual groundwater conditions of the study area. In addition to the cation concentrations, the concentration of major anions viz. $\text{HCO}_3^- = 250 \text{ mg/l}$, $\text{SiO}_2 = 15 \text{ mg/l}$ were also included. The concentration of PO_4^{3-} , which has highest effect on the adsorption capacity, was varied from 0.5 to 3 mg/l. The competition of adsorption sites for As with other anions as shown (Fig 7a-7b). The decrease in the adsorption capacities observed for initial As(V) $500 \mu\text{g/l}$ were 22%, 18% and 15% for the samples C_50, C_70 and C_150 respectively. With initial concentration of $300 \mu\text{g/l}$ decreased in adsorption were 31%, 26% and 18% respectively due to the competitive anions.

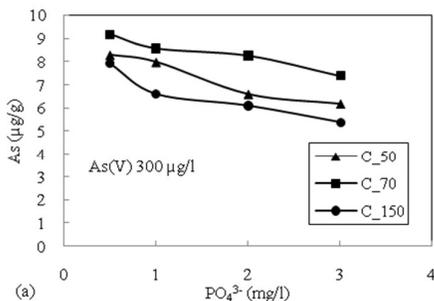


Fig. 7a. Combined effect of anions on adsorption of As(V) with initial concentration of $300 \mu\text{g/l}$ for sediment samples with increasing phosphate (PO_4^{3-}).

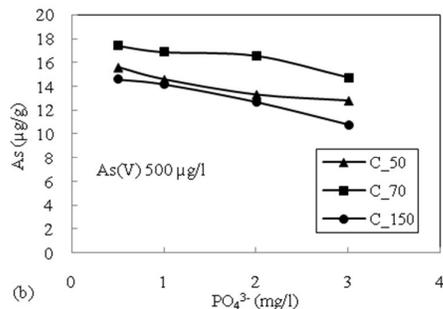


Fig. 7b. Combined effect of anions on adsorption of As(V) with initial concentration of $500 \mu\text{g/l}$ for sediment samples with increasing phosphate (PO_4^{3-}).

3.2 Sorption Kinetic of Arsenic

The adsorption process of As was found to be rapid. It was found that about 80% of total As adsorption was observed at initial 30 minutes.

Elovich adsorption kinetic model was found to be the best suitable kinetic model to describe the adsorption behaviour of As on the sediment. The model parameters were calculated from the linear plot of q_t versus $\ln(t)$. The Elovich constants a and b are defined as initial rate constant, ' a ' represents the rate of chemisorptions at zero coverage ($\mu\text{g/g min}$) and ' b ' is the extent of surface coverage and activation energy for chemisorptions ($\text{g}/\mu\text{g}$) has been tabulated (Table 3).

Similar rapid initial adsorption process was reported by various researchers^{16,23} on natural geological materials. Goh and Lim (2004)¹⁶ analyzed the tropical soil from Singapore and reported the Elovich model parameter for As(V) as, $a = 4.3\text{E}03$ and $b = 0.0366$ with $r^2 = 0.995$ and As(III) $a = 4.78\text{E}02$ and $b = 0.0516$ with $r^2 = 0.985$. The values obtained from our experiments (Table 3) revealed that there is no consistency in the values of Elovich coefficients for the sediment samples. Similar inconsistencies for the Elovich coefficient have been reported by various authors and sometimes, apparently abnormal values are also found³⁷.

Table 3. Regression analysis results of the Elovich kinetic model for As (III) and As(V) with initial concentrations of $300 \mu\text{g/l}$ and $500 \mu\text{g/l}$.

| As Species | Initial Conc. | parameters | C_50 | C_70 | C_150 |
|------------|---------------------|---------------------------------|----------|----------|----------|
| As(III) | 300 $\mu\text{g/l}$ | $a(\mu\text{g}/(\text{g min}))$ | 2.72E+01 | 1.21E+01 | 5.52E+02 |
| | | $b(\text{g}/\mu\text{g})$ | 1.62 | 1.12 | 1.9 |
| | | r^2 | 0.97 | 0.97 | 0.88 |
| As(V) | 300 $\mu\text{g/l}$ | $a(\mu\text{g}/(\text{g min}))$ | 7.73E+05 | 1.59E+05 | 7.74E+09 |
| | | $b(\text{g}/\mu\text{g})$ | 2.15 | 1.76 | 2.98 |
| | | r^2 | 0.89 | 0.94 | 0.91 |

The heterogeneity of sediments suggested pore diffusion or intra-particle diffusion to play a significant role along with surface adsorption. The plots of q_t versus $t^{0.5}$ (Fig 8) do not pass through the origin, but the straight line observed confirms the presence of intraparticle diffusion. A deviation from the origin shows that intraparticle transport is not the only rate limiting step. The large intercept in the plot indicates the greater contribution of the surface sorption in the rate controlling step. Table 4 showed the various parameters of Intraparticle diffusion models for various sediments. This reveals that the mechanism of metal ion adsorption by sediments is complex and both the surface adsorption as well as the intraparticle diffusion contributes to the rate determining step.

Table 4: Intra-particle diffusion adsorption model parameters for initial As(V) concentrations of $300 \mu\text{g/l}$ and $500 \mu\text{g/l}$.

| As ($\mu\text{g/l}$) | ID | $K_{id} (\mu\text{g}/(\text{g min}^{0.5}))$ | C ($\mu\text{g/g}$) | r^2 |
|------------------------|-------|---|-----------------------|-------|
| As(III) 300 | C_50 | 0.096 | 3.81 | 0.86 |
| As(III) 300 | C_70 | 0.412 | 4.38 | 0.94 |
| As(III) 300 | C_150 | 0.086 | 4.86 | 0.89 |

| | | | | |
|-------------|-------|-------|-------|------|
| As(III) 500 | C_50 | 0.054 | 4.39 | 0.94 |
| As(III) 500 | C_70 | 0.06 | 8.95 | 0.79 |
| As(III) 500 | C_150 | 0.033 | 4.95 | 0.66 |
| As(V) 300 | C_50 | 0.06 | 7.85 | 0.71 |
| As(V) 300 | C_70 | 0.088 | 8.488 | 0.86 |
| As(V) 300 | C_150 | 0.045 | 8.91 | 0.63 |
| As(V) 500 | C_50 | 0.079 | 14.37 | 0.83 |
| As(V) 500 | C_70 | 0.134 | 14 | 0.87 |
| As(V) 500 | C_150 | 0.107 | 14.01 | 0.62 |

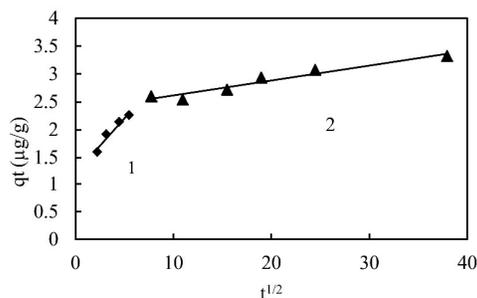


Fig. 8. Intra-particle diffusion model for C_50 sample with two linear segment for initial As(III) 300µg/l.

The multi linearity of the plot (Fig 8) shows that different mechanism of adsorption takes place for sample C_50. The initial part was attributed to the surface adsorption occurring instantaneously, while the gentle slope part was attributed to intraparticle diffusion, which was slow and likely to be rate-controlled^{36,37,48}.

3.3 Oxidation of As(III) to As(V)

The As(III) displayed varying transformation rates depending on the aquifer material. Since, sediments samples were found to adsorbed both As(III) and As(V), therefore, it was necessary to quantify redox speciation of arsenic in both dissolved and solid phases. The oxidation kinetics of As(III) for initial concentration 300 µg/l for three different types of sediments namely C_50, C_70 and C_150 are shown (Fig 9a-c). The sediment sample C_50 shows that the removal of aqueous As(III) was low (Fig 9a). The greater aqueous As(III) removal (25%) from the solution takes place via adsorption (higher solid As(III)) and lesser amount (20%) in oxidation of As(III) to As(V), which is in the form of solid As(V) in the sediment.

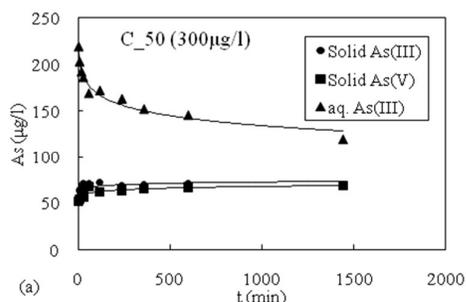


Fig. 9a. Oxidation kinetics of As(III) 300 µg/l for sediments sample C_50.

The oxidized sediment sample C_70 have highest capacity to oxidize As(III) to As(V) as shown (Fig 9b). The decrease in aqueous As(III) concentration with time was caused by a combination of oxidation and adsorption. The sediment of this zone has high concentration of Fe and Mn (Table 1). The Fe-oxides (amorphous and crystalline) have high affinity for As sorption^{18,20,41,42}. The aqueous As(III) removal from the solution was found to be highest among the sediment samples tested. It was observed that oxidation as compared to adsorption, was clearly the dominant mechanism for aqueous As(III) removal. From sample C_70 with an initial concentration of 300 µg/l of As(III), about 60% was removed via oxidation of As(III) to As(V) while 32% through adsorption onto the sediment samples respectively.

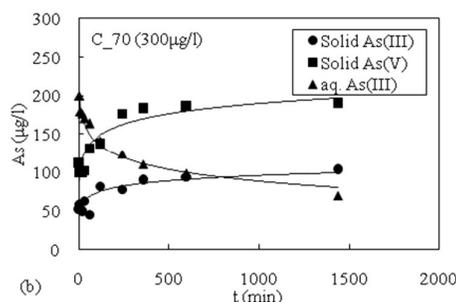


Fig. 9b. Oxidation kinetics of As(III) 300 µg/l for sediments sample C_70.

The sediment sample C_150 removal mechanism of As(III) from solution is shown (Fig 9c). Sediment sample C_150 was found to have higher aqueous As(III) removal via oxidation and lower amount of adsorption. For an 300 µg/l of As(III) concentration, the oxidation of As(III) to As(V) accounted 27% whereas the adsorption of As(III) onto the aquifer material accounted to about 23%.

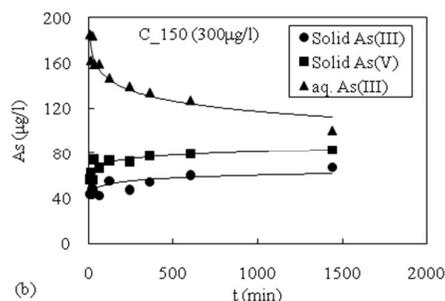


Fig. 9c. Oxidation kinetics of As(III) 300 µg/l for sediments sample C_150.

In all the samples, mass balance was within $\pm 15\%$ of the initial As(III) concentration. This suggested that 15 minutes of 0.2M oxalic acid extraction is an effective method for desorption of As species from aquifer materials^{17,31}. Oxidation of As(III) to

As(V) by Mn-oxides in natural sediments have been reported^{17,31,49}.

Thus, tapping water from the zone of oxidized sediment of relatively good thickness will be able to reduce the As concentration in the groundwater. Since, As chemistry is governed by complex sets biogeochemical processes therefore, quantification of As desorbed from the aquifer leading to groundwater As concentration requires more advanced experimental studies and extensive field investigations to develop a model and assess the attenuation capacity of the sediments for As.

Comparison with Bengal Delta and Red River Delta, Vietnam where intensive studies on the geochemical modelling using surface complexation model have been published on Bengal Basin²² and in the Red River floodplains of Vietnam²¹. Biswas et al. (2014)²² reported the role of competing ions in As mobilization process. They observed that reductive dissolution of only Fe-oxyhydroxide cannot explain higher As concentration in the groundwater of Bengal Basin. The As release by reductive dissolution Fe-oxyhydroxide might have been re-adsorbed in sediment materials. Biswas et al. (2014)²² account the reductive dissolution followed by competitive ion adsorption, mainly (PO_4^{3-}) responsible for higher concentration of As in the aquifer of Bengal Basin. Jessen et al. (2012)²¹ on goethite found that As(V) adsorbs much stronger than As(III) and PO_4^{3-} and Fe(II) forms the main competing species in the Red River flood plains, Vietnam. Similarly, this paper discussed the role of competing ions in the release of As in the Brahmaputra floodplains of Assam. The results also indicated that PO_4^{3-} is the main competing ions for surface adsorption on the sediments. And among the three generic sediments found in the area, more oxidized sediments have the highest capacity for As adsorption. The attenuation of arsenic occurs when As(III) gets oxidized to As(V) followed by adsorption on the sediments. Therefore, targeting safe aquifer in the area should incorporate the color identification of sediments as the depth of aquifer media vary to large extent in vertical direction.

Conclusions

The batch sorption studies for attenuation of As in groundwater was performed on sediment samples viz. C_50, C_70 and C_150 representing common sedimentary deposits in the area of high As contaminated areas. All the sediment samples were able to adsorb As(V) and As(III) at pH where groundwater was observed. The minor reduction in adsorption of As(V) with increasing pH (6 – 8.5) suggested electrostatic repulsion due to soil surface charge density. Small increase in the adsorption of As(III) with increasing pH could be due to relatively lesser negative charge, which prohibited electrostatic repulsion between As(III) and the hydroxylic functional group. As(V) exhibit higher adsorption than As(III) species for all types of sediments. Freundlich adsorption isotherm fits relatively better for both As(III) and As(V).

The oxidized sediment sample C_70 demonstrated highest As adsorption capacity, as this sample has higher Fe and Mn

content. PO_4^{3-} was found to have highest competition with As(V) adsorption sites on the reduced sediment (C_50) as well as moderately oxidized sediment (C_150), and showed lesser effects on oxidized sediment (C_70). The competition of adsorption sites for the anions considered generally followed the order $\text{PO}_4^{3-} > \text{SiO}_2 > \text{HCO}_3^-$. The combined effects of anions showed highest reduction in the adsorption capacities for all the sediment samples. The adsorption kinetics could be best described with Elovich kinetics model. Significant correlation was observed for intra-particle diffusion model due to heterogeneity of the sediments. The rate determining step was found to be controlled mainly by surface sorption and partly through intra-particle diffusion.

Transformation of As(III) to As(V) not only decrease the toxicity but also enhances As removal from drinking water and sequestration to soils and sediments. The oxidation of As(III) to As(V) experiment showed that aqueous As(III) oxidation to solid As(V) in the oxidative sites of the sediments was the dominant As removal mechanism for oxidized sediment (C_70) and moderately oxidized sediment (C_150). The direct adsorption of aqueous As(III) on the adsorptive sites as solid As(III) was main process of As removal for reduced sediment sample C_50.

The findings of the study can be used for exploring integrated mitigation strategy for As contamination e.g. through targeting oxidizing sediments by placing well screen at specific depths or to target specific aquifers with As free sediment architecture to obtain As safe drinking water for rural communities. Thus suggested that natural aquifer materials might make natural attenuation of As viable sources of drinking water.

References

- 1 CGWB-Central Ground Water Board, 2004 "Groundwater Resources of Assam" CGWB, North East Region, Ministry of Water Resource, Guwahati.
- 2 Breit, G.N., Whitney, J.W., Foster, A.L., Stollenwerk, K.G., Yount, J.C., Welch, A.H., 2003. Geochemical changes affecting arsenic in the sediment of the Ganges-Brahmaputra-Meghna river system. Prog Abstr Geol Soc Am Ann Mtng, Seattle, WA.
- 3 Nickson, R., Sengupta, C., Mitra, P., Dave, S. N., Banerjee, A. K., Bhattacharya, A., 2007. Current knowledge on the distribution of arsenic in groundwater in five states of India. Journal of Environmental Science and Health Part A, 42: 1707–1718.
- 4 Harvey, C.F., Swartz, C.H., Badruzzaman, A.B.M., Keon, B.N., Yu, W., Ashraf, A.M., Jay, J., Beckie, R., Niedan, V., Brabander, D., Oates, P.M., Ashfaq, K.N., Islam, S., Hemond, H.F., Ahmed, M.F., 2002. Arsenic mobility and groundwater extraction in Bangladesh. Science 298, 1602–1606.
- 5 Harvey, C.F., Swartz, C.H., Badruzzaman, A.B.M., Keon, B.N., Yu, W., Ali, M.A., 2005. Groundwater arsenic contamination on the Ganges delta: biogeochemistry, hydrology, human perturbations, and human suffering on a large scale. C R Geoscience 337, 285–96.
- 6 Biswas, A., Nath, B., Bhattacharya, P., Halder, D., Kundu, A.K., Mandal, U., Mukherjee, A., 460 Chatterjee, D., Mörth, C. M., Jaks, G., 2012. Hydrogeochemical contrast between brown 461 and grey sand aquifers in shallow depth of Bengal Basin:

- Consequences for sustainable 462 drinking water supply. *Sci. Total Environ.* 431, 402-412.
- 7 Robinson, C., von Bromssen, M., Bhattacharya, P., Haller, S., Biven, A., Hossain, M., Jacks, G., Ahmed, K.M., Hasan, M.A., Thunvik, R., 2011. Dynamic of arsenic adsorption in the targeted arsenic-safe aquifers in Matlab, south-eastern Bangladesh: Insight from experimental studies. *Applied Geochemistry* 26, 624-635.
 - 8 Van-Bromssen, M., Larsson, S.H., Bhattacharya, P., Hasan, M.A., Ahmed, K.M., Jakariya, 599 M., Sikder, M.A., Sracek, O., Bivén, A., Doušová, B., Patriarca, C., Thunvik, R., Jacks, G., 600 2008. Geochemical characterisation of shallow aquifer sediments of Matlab Upazila, 601 Southeastern Bangladesh – implications for targeting low-As aquifers. *J. Cont. Hydrol.* 99, 602 137-149.
 - 9 McArthur, J.M., Ravenscroft, P., Safiullah, S., Thirlwall, M.F., 2001. Arsenic in groundwater: testing pollution mechanisms for sedimentary aquifers in Bangladesh. *Water Resources Research*, 37,109–117.
 - 10 McArthur, J.M., Nath, B., Banerjee, D.M., Purohit, R., Grassineau, N., 2011. Palaeosol Control on Groundwater Flow and Pollutant Distribution: The Example of Arsenic. *Environmental Science and Technology* 45, 1376-1383.
 - 11 Sailo, L., and Mahanta, C., 2013. Hydro-geochemical factors affecting the mobilization of As into the groundwater of the Brahmaputra alluvial plains of Assam, Northeast India. *Environmental Science.: Processes Impacts*, Vol 15 pp 1775–1782.
 - 12 Bhattacharya, P., Chatterjee, D., Jacks, G., 1997. Occurrence of arsenic contaminated groundwater in alluvial aquifers from Delta plains, Eastern India: options for safe drinking water supply. *Water Resource Development* 13, 79–92.
 - 13 Postma, D., Jessen, S., Minh Hue, Duc, M. T., Koch, C.B., N.T., Viet, P.H., Nhan, P.Q., Larsen, F., 2010. Mobilization of arsenic and iron from Red River floodplains sediments, Vietnam. *Geochimica et Cosmochimica Acta* 74, 3367-3381.
 - 14 Wang, S., Mulligan, C.N., 2006. Natural attenuation processes for remediation of arsenic contaminated soils and groundwater. *Journal of Hazardous Materials* B138:459-470.
 - 15 Wang, Y., Deng, Y., 2009. *Environmental Geochemistry of High-Arsenic Aquifer Systems*. In: Wang, L.K., Chen, J.P., Hung, Y.T., Shammis, N.K., editors. *Heavy Metal in the Environment*. Taylor and Francis group, CRC press.
 - 16 Goh, K.H., Lim, T.T., 2004. Geochemistry of inorganic arsenic and selenium in a tropical soil: effect of reaction time, pH, and competitive anions on arsenic and selenium adsorption. *Chemosphere* 55, 849-859.
 - 17 Stollenwerk, K.G., Breit, G.N., Welch, A.H., Yount, J.C., Whitney, J.W., Foster, A.L., Uddin, M.N., Majumder, R.K., Ahmed, N., 2007. Arsenic attenuation by oxidized aquifer sediments in Bangladesh. *Science of the Total Environment* 379, 133-150.
 - 18 Manning, B.A., Goldberg, S., 1997. Adsorption and stability of arsenic at the clay mineral–water interface. *Environmental Science and Technology* 31, 2005–2011.
 - 19 Goldberg, S., 2002. Competitive adsorption of arsenate and arsenite on oxides and clay minerals. *Soil Science Society American Journal* 66, 413-421.
 - 20 Dixit, S., Hering, J.G., 2003. Comparison of arsenic(V) and arsenic(III) sorption onto iron oxide minerals: implications for arsenic mobility. *Environmental Science and Technology* 37, 4182–4189.
 - 21 Jessen, S., Postma, D., Larsen, F., Nhan, P.Q., Hoa, L.Q., Trang, P.T.K., Long, T.V., Viet, 512 P.H., Jakobsen, R., 2012. Surface complexation modeling of groundwater arsenic mobility: 513 Results of a forced gradient experiment in a Red River flood plain aquifer, Vietnam. 514 *Geochim. Cosmochim. Acta.* 98, 186-201.
 - 22 Biswas, A., Gustafsson, J.P., Neidhardt, H., Halder, D., Kundu, A.K., Chattarjee, D., Berner, Z., Bhattacharya, P., 2014. Role of competing ions in the mobilization of arsenic in groundwater of Bengal Basin: Insight from surface complexation modelling. *Water Research* 55, 30-39.
 - 23 Barrachina, C.A.A., Carbonell, F. B., Beneyto J. M., 1996. Kinetics of arsenite sorption and desorption in Spanish soils. *Commun. Soil Sci. Plant. Anal.* 27: 3101-3117.
 - 24 Acharyya, S.K., Lahiri, S., Raymahashay, B.C., Bhowmik, A., 2000. Arsenic toxicity of groundwater in parts of the Bengal basin in India and Bangladesh: the role of Quaternary stratigraphy and Holocene sea-level fluctuation. *Environmental Geology* 39, 1127-1137.
 - 25 Anawar, H.M., Akai, J., Komaki, K., Terao, H., Yoshioka, T., Ishizuka, T., Safiullah, S., Kato, K., 2003. Geochemical occurrences of arsenic in groundwater of Bangladesh: sources and mobilization processes. *Journal of Geochemical Exploration* 77, 109–131.
 - 26 Berg, M., Trang, P.T.K., Stengel, C., Buschmann, J., Viet, P.H., Dan, N.V., Giger, W., Stuben, D., 2008. Hydrological and Sedimentary controls leading to arsenic contamination of groundwater in the Hanoi area, Vietnam: The impact of iron-arsenic ratios, peat, river bank deposits and excessive groundwater abstraction. *Chemical geology* 249, 91-112.
 - 27 Sracek, O., Bhattacharya, P., Jacks, G., Gustafsson, J.P., von Brömssen, M., 2004. Behavior 573 of arsenic and geochemical modeling of arsenic enrichment in aqueous environments. 574 *Appl. Geochem.* 19, 169-180.
 - 28 Swartz, C.H., Blute, N.K., Badruzzman, B., Ali, A., Brabander, D., Jay, J., Besancon, J., Islam, S., Hemond, H.F., Harvey, C., 2004. Mobility of arsenic in a Bangladesh aquifer: inferences from geochemical profiles, leaching data, and mineralogical characterization. *Geochimica et Cosmochimica Acta* 68, 539–4557.
 - 29 Postma, D., Larsen, F., Nguyen, T.M.H., Mai, T.D., Pham, H.V., Pham, Q.N., Jessen, S, 560 2007. Arsenic in groundwater of the Red River floodplain, Vietnam: Controlling 561 geochemical processes and reactive transport modeling. *Geochim. Cosmochim. Acta.* 71, 562 5054-5071.
 - 30 Stachowicz, M., Hiemstra, T., Van Riemsdijk, W.H., 2008. Multi-competitive interactions of 578 As(III) and As(V) oxyanions with Ca²⁺, Mg²⁺, PO₄³⁻, and CO₃²⁻ ions on goethite. *J. Colloid 579 Interface Sci.* 320, 400-414.
 - 31 Amirbahman, A., Kent, D. B., Curtis, G. P., Davis, J. A., 2006. Kinetics of sorption and abiotic oxidation of arsenic(III) by aquifer materials. *Geochimica et Cosmochimica Acta* 70, 533–547.
 - 32 De Vitre R., Belzile N., and Tessier A. (1991) Speciation and adsorption of arsenic on diagenetic iron oxyhydroxides. *Limnol. Oceanogr.* 36, 7, 1480–1485
 - 33 Oscarson, D.W., Huang, P.M., Defosse, D., Herbillion, A., 1981. Oxidative power of Mn(IV) and Fe(III) oxides with respect to As(III) in terrestrial and aquatic environments. *Nature* 291, 50-51.
 - 34 Oremland, R.S., Stolz, J.F., 2003. The ecology of arsenic. *Science* 300, 939-944.
 - 35 Sailo, L., and Mahanta, C., 2014. Arsenic mobilization in the Brahmaputra plains of Assam: groundwater and sedimentary controls. *Environmental Monitoring Assessment (2014) Vol 186:* 6805–6820.
 - 36 Wu, F.C., Tseng, R.L., Juang, R.S., 2009. Initial behavior of intraparticle diffusion model used in the description of adsorption kinetics. *Chem. Eng. J.* 153 (2009), 1–8.
 - 37 Gupta, S.S., Bhattacharyya, K.G., 2011. Kinetics of adsorption of metal ions on inorganic materials: A review. *Advances in colloid and Interface Science* 162, 39-58.

- 1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
- 38 Weber, W.J., Morris, C.J. 1963. Kinetics of adsorption on carbon from solution, *J. San. Eng. Div. Proc. Anal. Soc. Civil Eng.* 89, SA2 31.
- 39 Febrianto, J., Kosasih, A.N., Sunarso, J., Ju, Y., Indraswati, N., Ismadji, S., 2009. Equilibrium and kinetic studies in adsorption of heavy metals using biosorbent: A summary of recent study. *Journal of Hazardous Materials*, 162: 616-645.
- 40 Freundlich, H. 1906. Über die adsorption in lusungen. *Journal of Physical Chemistry*. 57: 385 (in German).
- 41 Smedley, P.L., Kinniburgh, D.G., 2002. A review of the source, behavior and distribution of arsenic in natural waters. *Applied Geochemistry* 17, 517–68.
- 42 Arai, Y., Sparks, D.L., Davis, J.A., 2005. Arsenate adsorption mechanisms at the allophane–water interface. *Environmental Science and Technology*, 39, 2537–2544.
- 43 Meng, X.G., Bang, S., Korfiatis, G.P., 2000. Effects of silicate, sulfate and carbonate on arsenic removal by ferric chloride. *Water Research* 34, 1255-1261.
- 44 Stumm, W., 1992. *Chemistry of the solid-water interface*. Wiley and Sons, New York.
- 45 Zheng, Y., van Geen, A., Stute, M., Dhar, R., Mo, Z., Cheng, Z., Horneman, A., Gavrieli, I., Simpson, H.J., Versteeg, R., Steckler, M., Grazioli-Venier, A., Goodbred, S., Shahnewaz, M., Shamsudduha, M., Hoque, M.A., Ahmed, K.M., 2005. Geochemical and hydrogeological contrasts between shallow and deeper aquifers in two villages of Arahazar, Bangladesh: implications for deeper aquifers as drinking water sources. *Geochimica et Cosmochimica Acta* 69, 5203–5218.
- 46 Eiche, E., Neumann, T., Berg, M., Weinman, B., van Geen, A., Norra, S., Berner, Z., Trang, P.T.K., Hung Viet, P., Stüben, D., 2008. Geochemical processes underlying a sharp contrast in groundwater arsenic concentrations in a village on the Red River delta, Vietnam. *Applied Geochemistry* 23, 3143–3154.
- 47 Appelo, C.A.J., Van-Der-Weiden, M.J.J., Tournassat, C., Charlet, L., 2002. Surface complexation of ferrous iron and carbonate on ferrihydrite and the mobilization of arsenic. *Environmental Science and Technology* 36, 3096–3103.
- 48 Ho, Y.S., Chiu, W.T., Hsu, C.S., Huang, C.T., 2004. Sorption of lead ions from aqueous solution using tree fern as a sorbent. *Hydrometallurgy* 73 (1–2), 55–61.
- 49 Han, X., Li, Y.L., Gu, J.D., 2011. Oxidation of As(III) by MnO₂ in the absence and presence of Fe(II) under acidic conditions. *Geochimica et Cosmochimica Acta* 75, 368-379.