# Treatment of Groundwater for Removal of Arsenic and Manganese

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# Presentation Outline

- Background
- Objectives
- Methodology
- Major Findings
- Conclusions

# BACKGROUND:

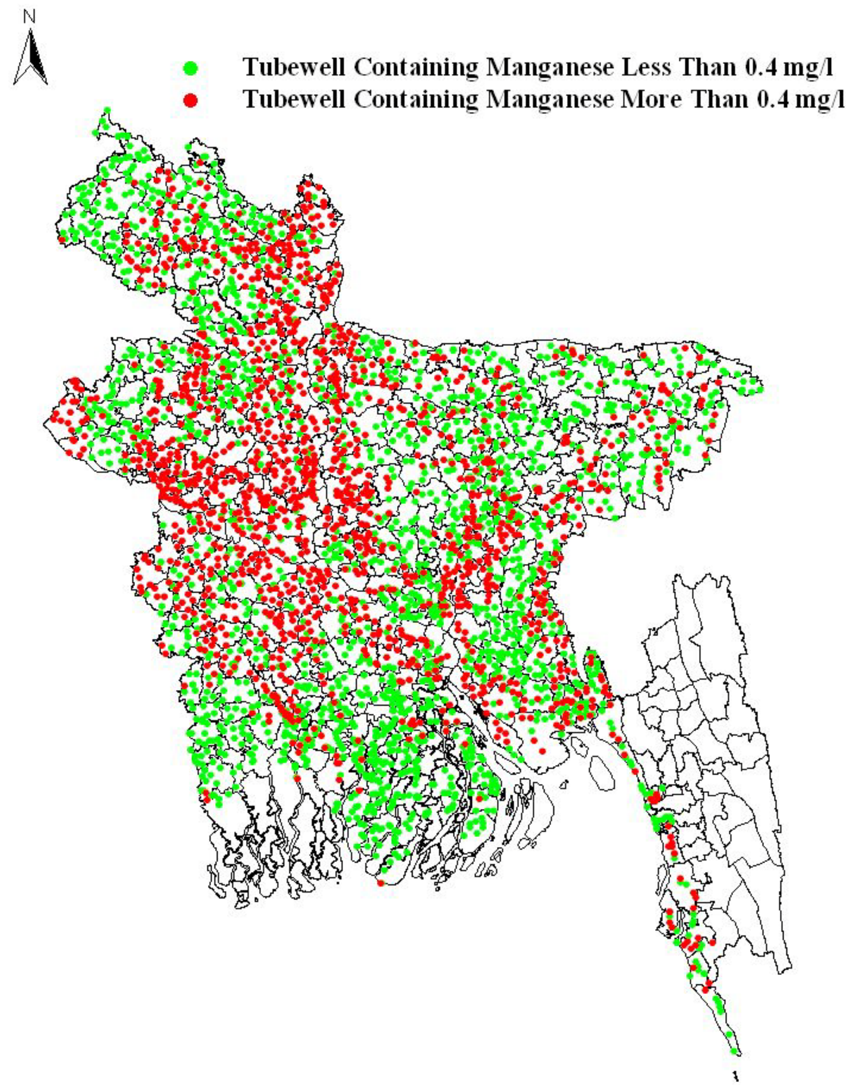
## Distribution of
## Mn and As
## in Groundwater

# Drinking Water Quality Standards for As and Mn

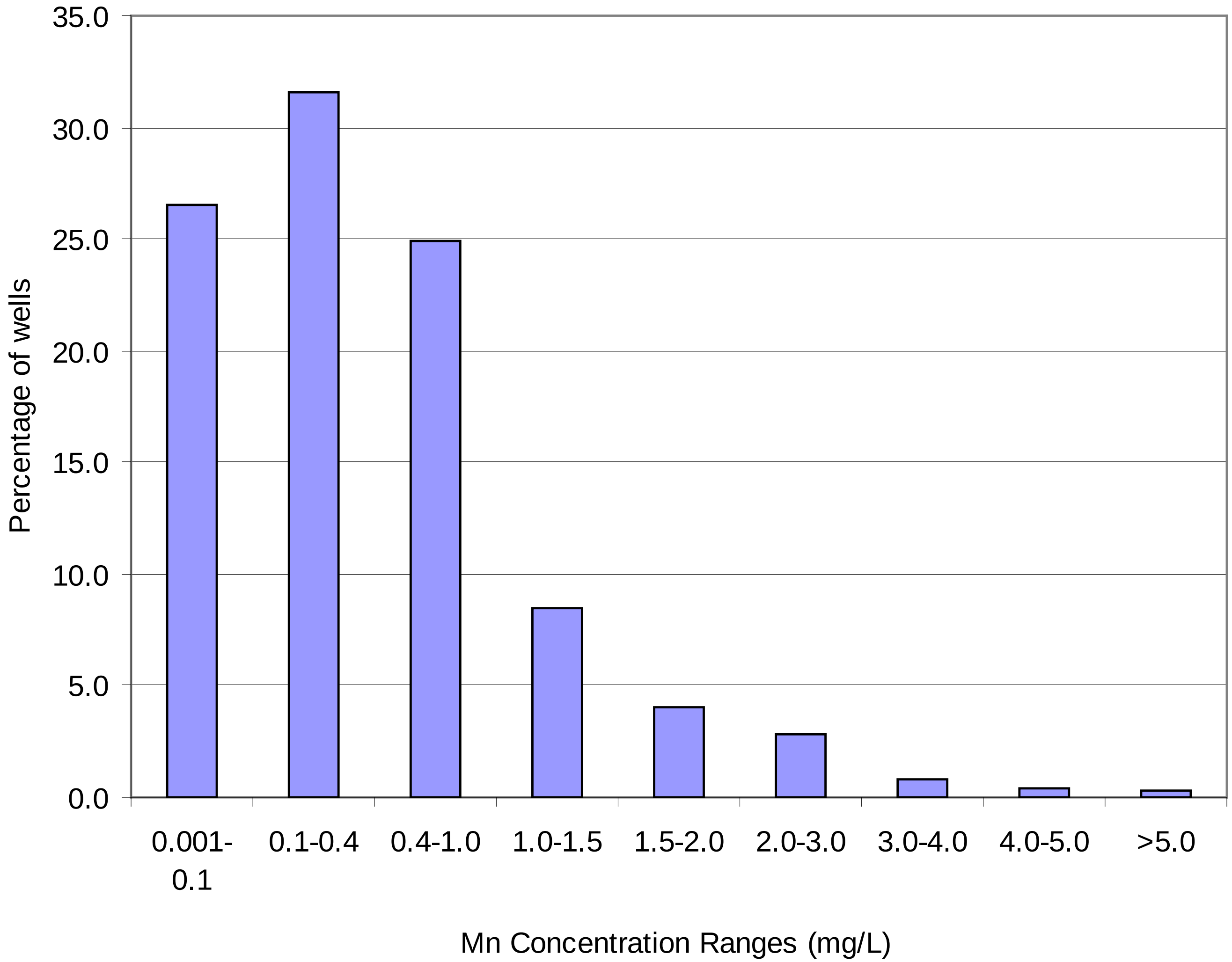
- **Arsenic (As):**
  - Bangladesh Standard: 0.05 mg/l (health-based)
  - WHO Guideline Value: 0.01 mg/l (health-based)

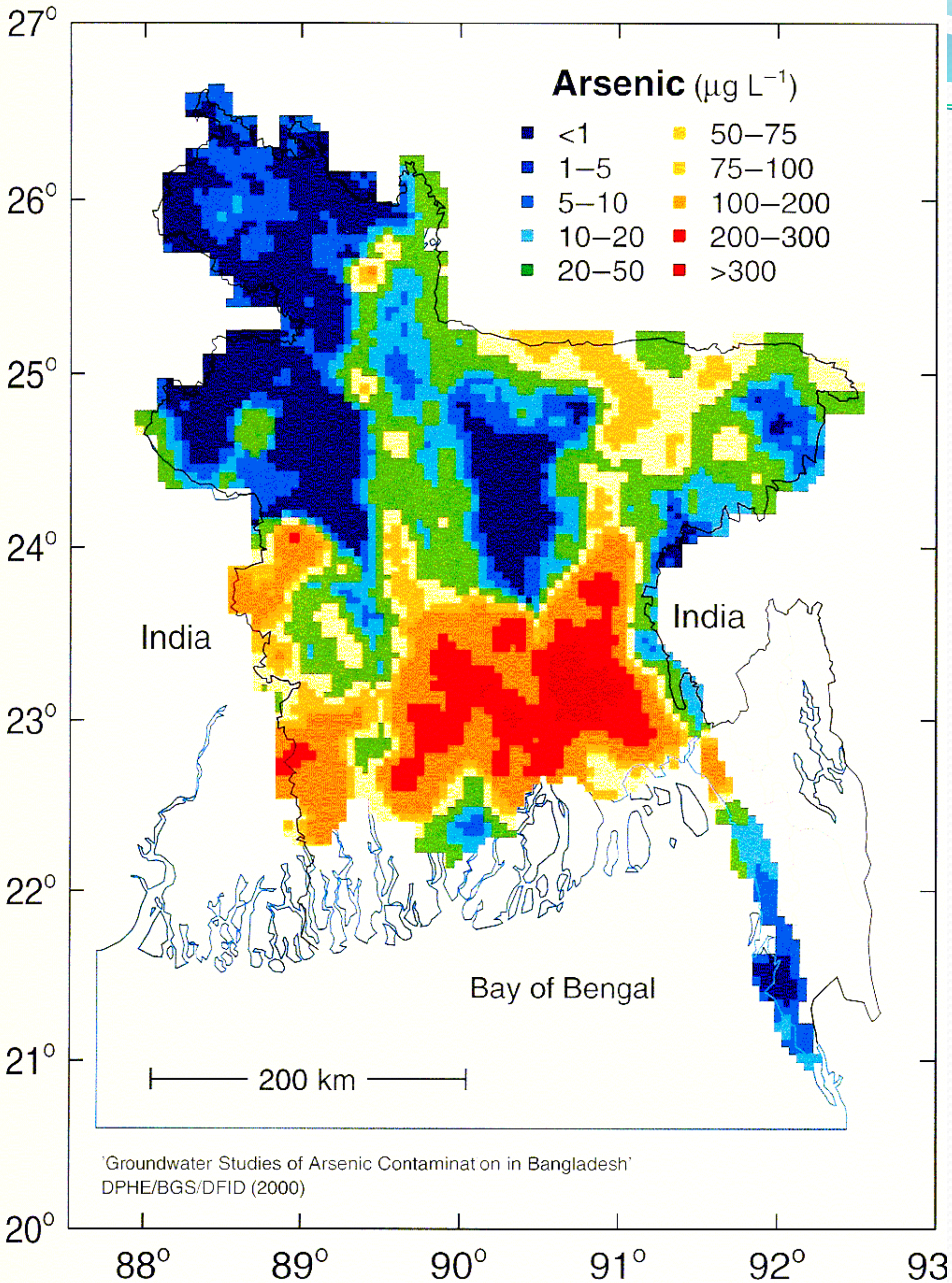
- **Manganese (Mn):**
  - Bangladesh Standard: 0.1 mg/l (aesthetic consideration)
  - WHO Guideline Value (2004): **0.4 mg/l** (health-based)

# Distribution of Mn in the Groundwater of Bangladesh



# Distribution of Mn Concentration in Well Water

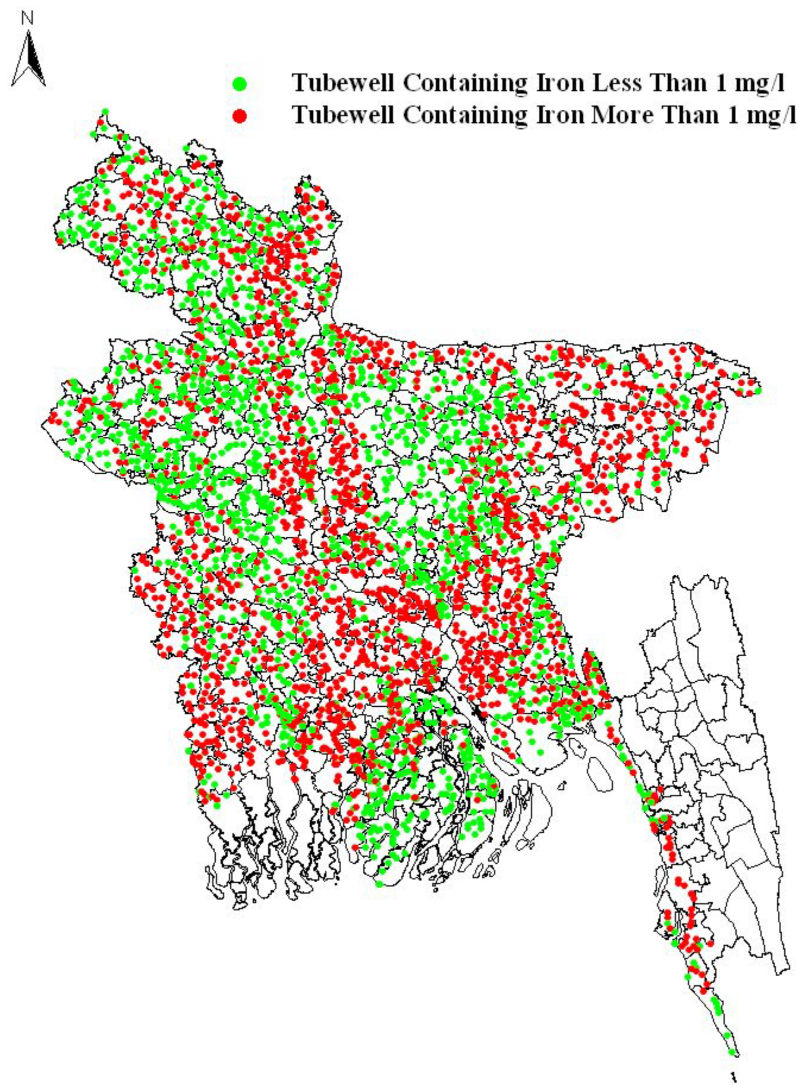




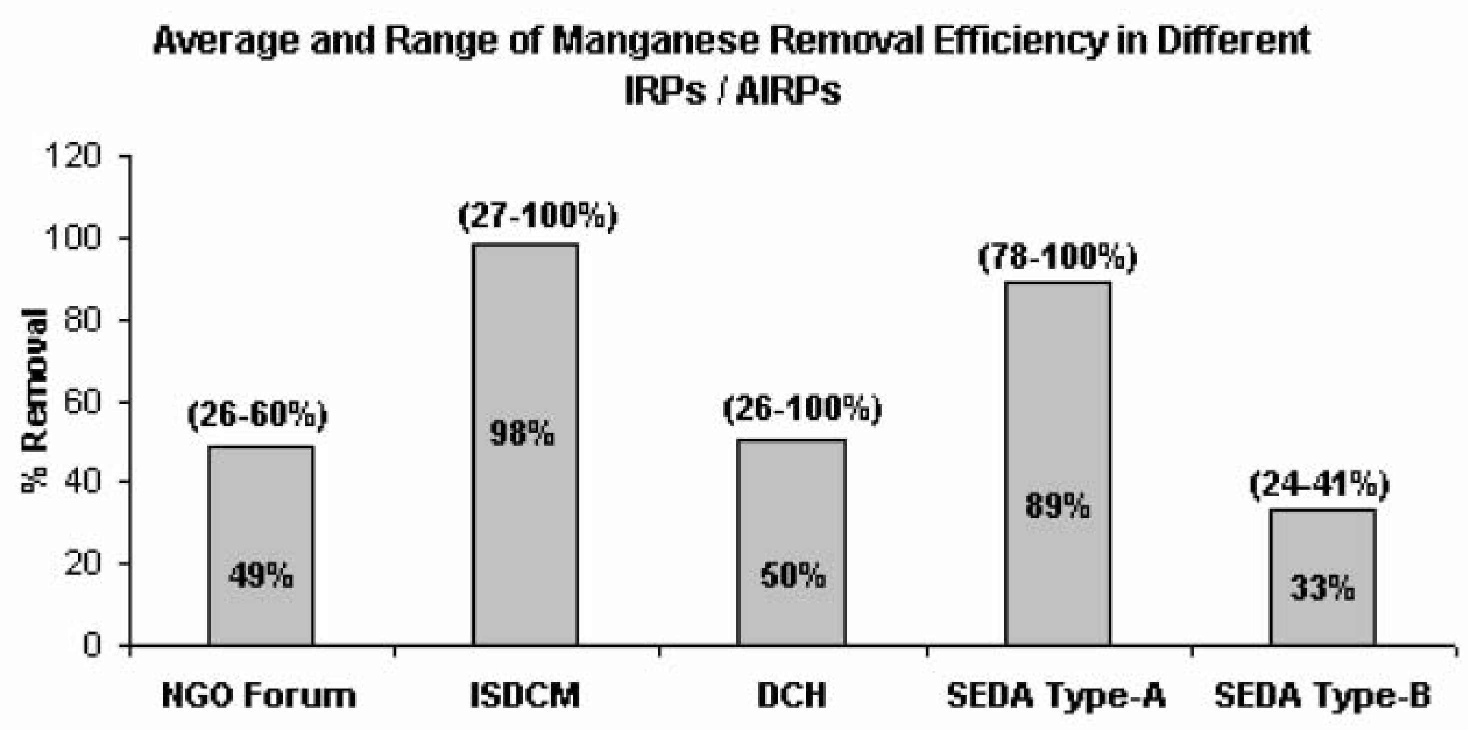

# *Arsenic in Groundwater:*

- **Shallow aquifer (< 100 m) primarily affected, which is widely used for <u>domestic purpose</u> through use of hand tubewells as well as for <u>irrigation</u>**
- **Out of 465 *upazilas* (sub-districts), 270 seriously affected**

# *Distribution of Fe in the groundwater of Bangladesh*



# BACKGROUND:
# Mn Removal in Community AIRPs:
**(BUET Study, funded by Unicef; 2005-06)**



# OBJECTIVES OF PRESENT STUDY

- Evaluation of performance of 3 types of Mn-oxide coated sand media for simultaneous removal of As and Mn. The Mn-oxide coated media included:

  - "Mn-coated sand" prepared by passing Mn-bearing water through a sand filter bed.
  - "Synthestic Mn-coated sand" prepared following the methods of Tilak (undated) and Merkle et al. (1997), using $Mn(NO_3)2.4H_2O$; NaOH; $H_2O_2$.
  - Commercially available "Green sand".

# *OBJECTIVES* (Contd.)

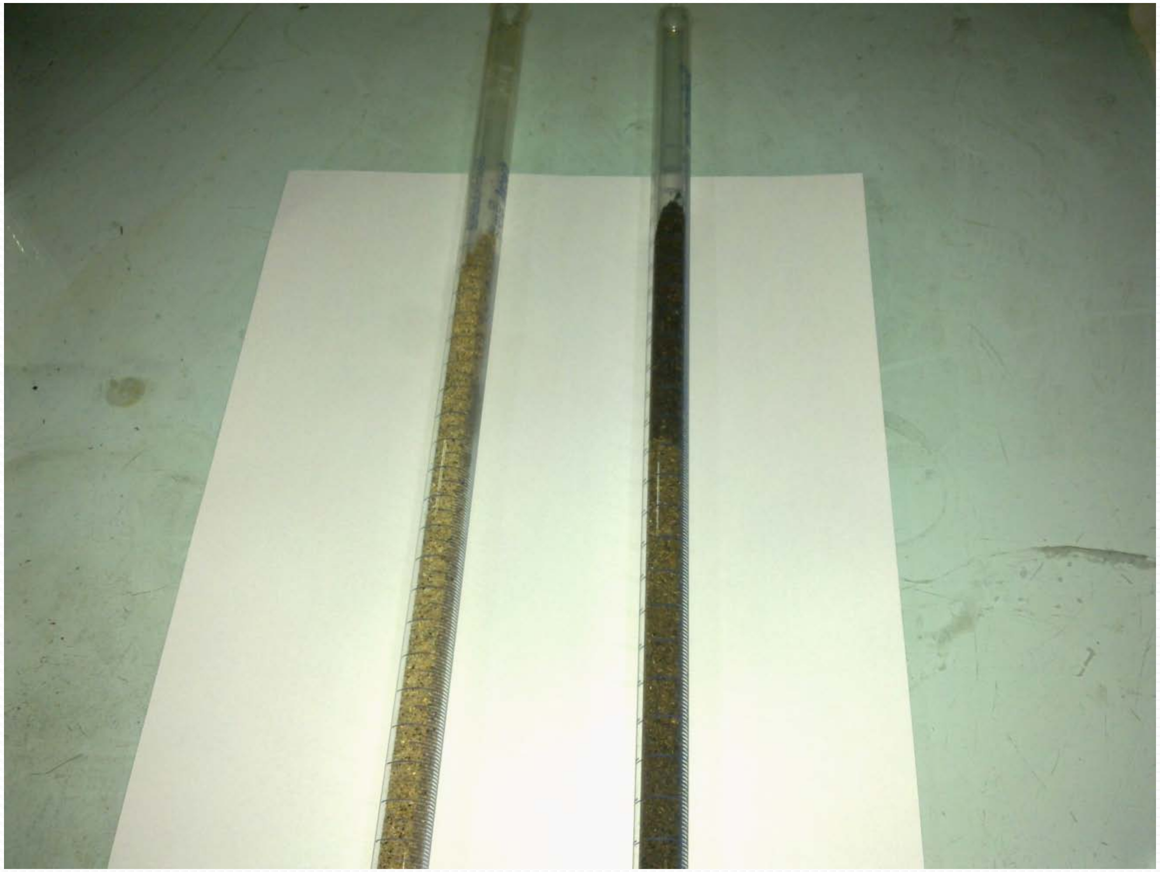
- Assessment of the characteristics of the filter media and process variables (e.g., media depth, flow rate, contact time) and water (i.e. initial concentrations, time, pH, bicarbonate, phosphate) on removal of Mn and As.
- Identification of the cause(s) of variable performance of selected existing community As and As-Fe removal plants in removing Fe, As and Mn.
- Development of criteria for optimal removal of Mn and As from natural groundwater in a treatment system.

# METHODOLOGY

# Preparation of "Mn-coated sand": Experimental Set Up

- Column x-section: 1 sq.cm.
- Filter depth: 43 cm
- Flow rate: 1 – 5 ml/min
- Contact time: 10.75 - 2.15 min
- Mn Concentration: 0.5-5.0 mg/l
- pH: 7.0 ± 0.10 (natural)

# *Formation of Mn oxide coating on sand*



- Sand grains turned dark due to formation of Mn-oxide coating
- Mn-coatings form primarily at the top of the column

# Preparation of Synthetic Mn-Oxide Coated Sand

- Following the methods of Tilak (undated) and Merkle et al. (1997), using $Mn(NO_3)_2.4H_2O_;$ NaOH; $H_2O_2$.
- 100 gm of the selected sand was taken in a glass tray
- 100 ml of $Mn(NO_3)_2.4H_2O$ solution (Mn: 10.5 g/l) was added to the tray and mixed thoroughly with the sand.
- 0.1N NaOH and 1:1 30% $H_2O_2$ were added to the tray until the pH of the mixture increased to about 9.0.
- As pH of solution gradually decreased, 0.1N NaOH was added to mixture 2 to 3 times, once every 2 hours, to raise the pH to about 9.0.
- The above process was repeated twice; sand in the tray was then air dried

# *Preparation of Synthetic Mn-Oxide Coated Sand*

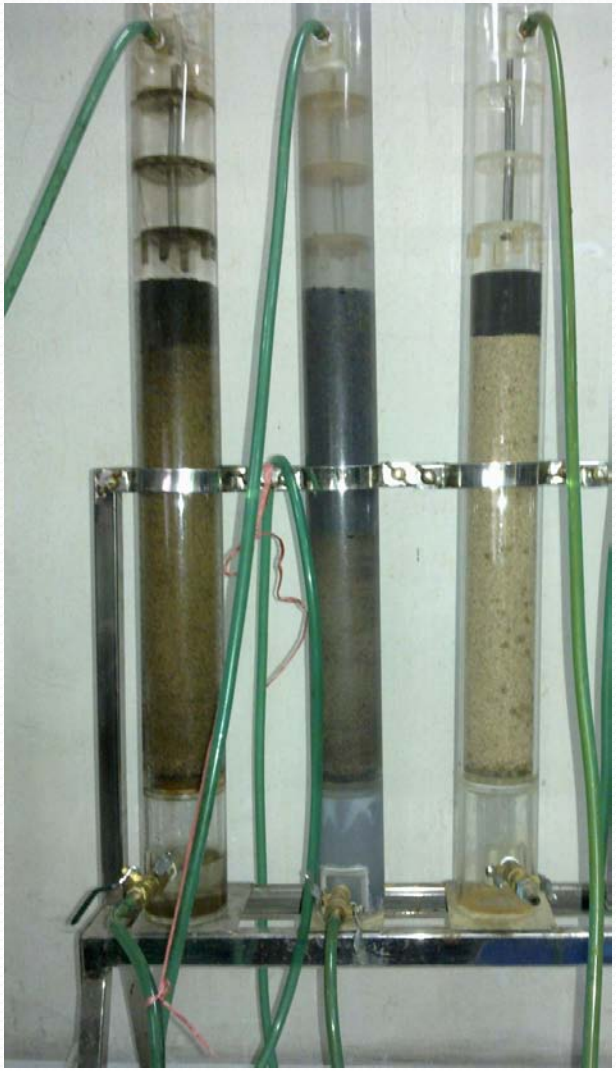
- Mn content of synthetic Sand: 25,250 mg/kg

# *Removal of Mn and As by: (a) Mn-coated Sand, (b) Synthetic Mn-coated Sand, (c) Green Sand*

- Column x-section: 28.2 sq.cm.*
- Total filter depth: 40 cm
- Mn-coated sand: Top 6 cm**
- Sylhet Sand: Bottom 30 cm
- Flow rate: 0.5 - 8 ml/sq.cm./min
  (14.1 ml/min to 225.6 ml/min)
- Mn Concentration: 4 mg/l
- pH: natural pH (around 7)

* 26.5 sq. cm. for Green Sand column

** up to 30 cm for Green sand



**Mn Content (mg/kg):**

- Mn-coated sand: 1480 (avg), 7550 (top)
- Synthetic Mn-coated sand: 25,250
- Green Sand: 14,400

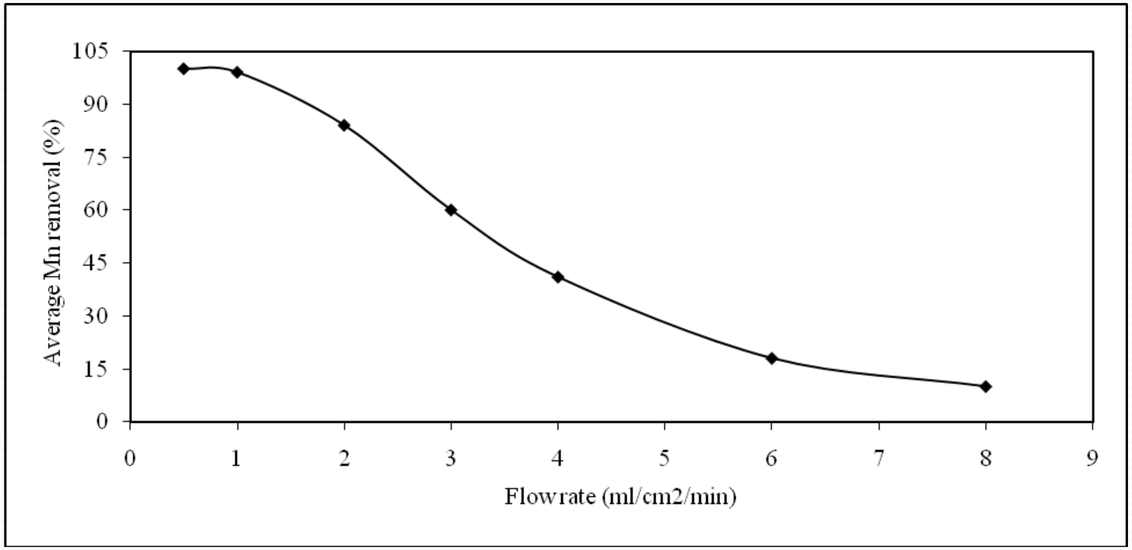
## *Removal of Mn and As by: (a) Mn-coated Sand, (b) Synthetic Mn-coated Sand, (c) Green Sand*

**Influent Water:**

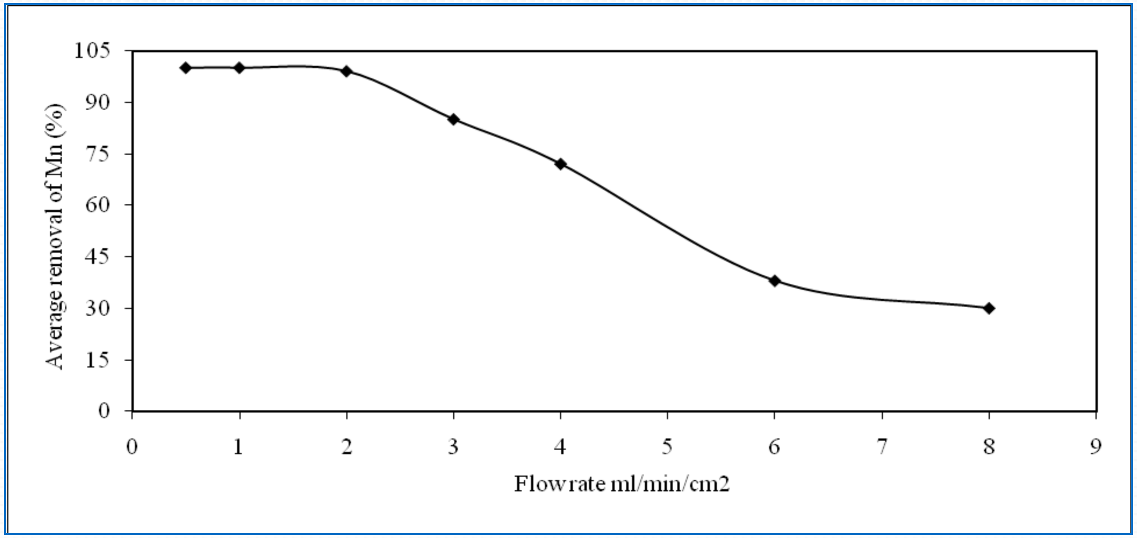
- **Amended Natural Groundwater**
- **pH: 7.0 ± 0.1**
- **Mn: 0.5 to 5.0 mg/l**
- **As: 100 to 500 μg/l**
- **Alkalinity: 50 to 500 mg/l as $CaCO_3$**
- **Phosphate: 1 to 10 mg/l**

# MAJOR FINDINGS

# Removal of Mn: Effect of Flow Rate/ Contact Time

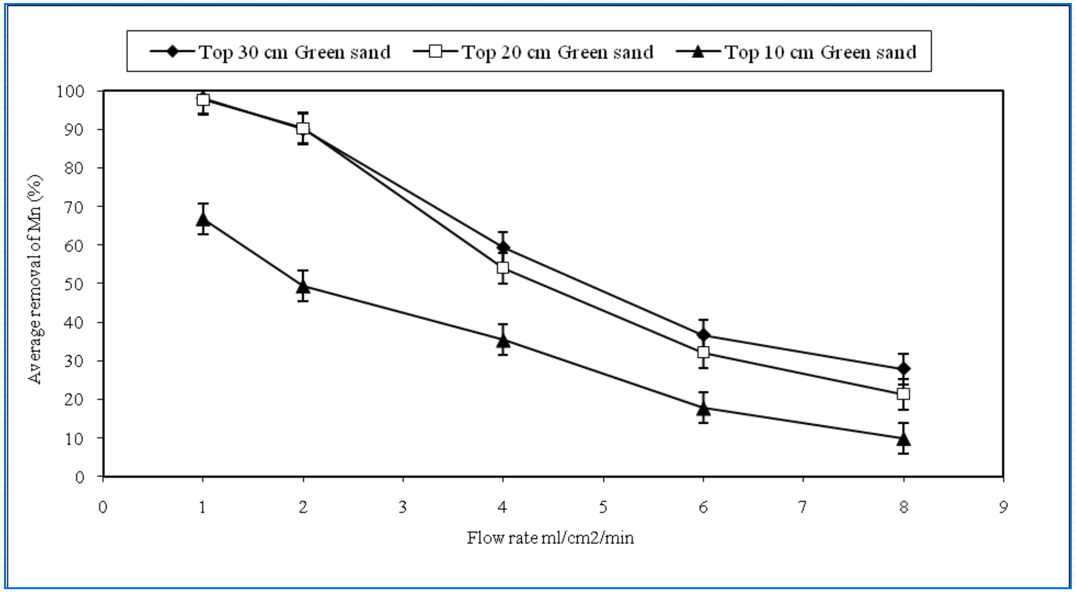



**Mn-coated sand**



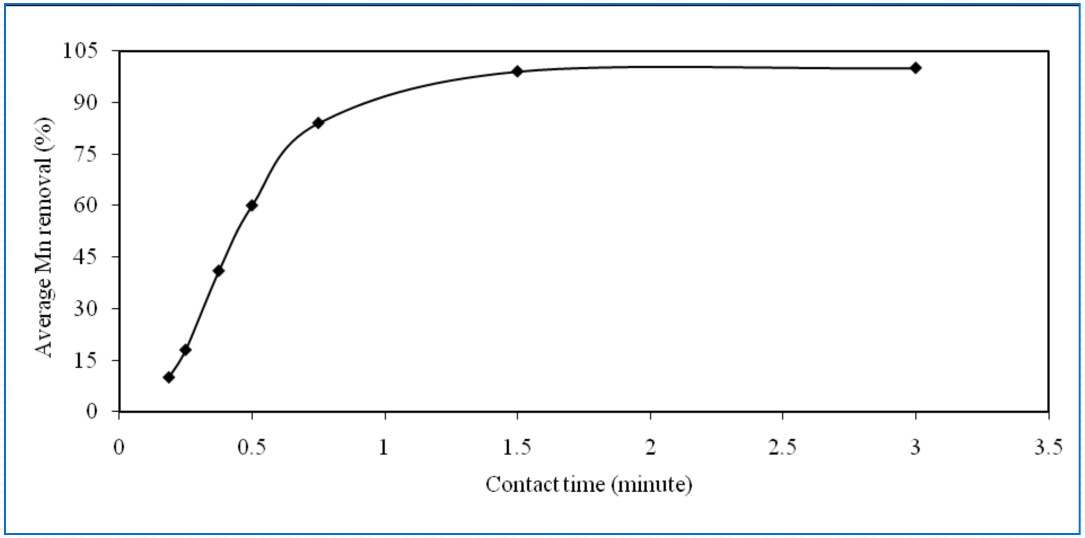

**Synthetic Mn-coated sand**

# Removal of Mn: Effect of Flow Rate/ Contact Time

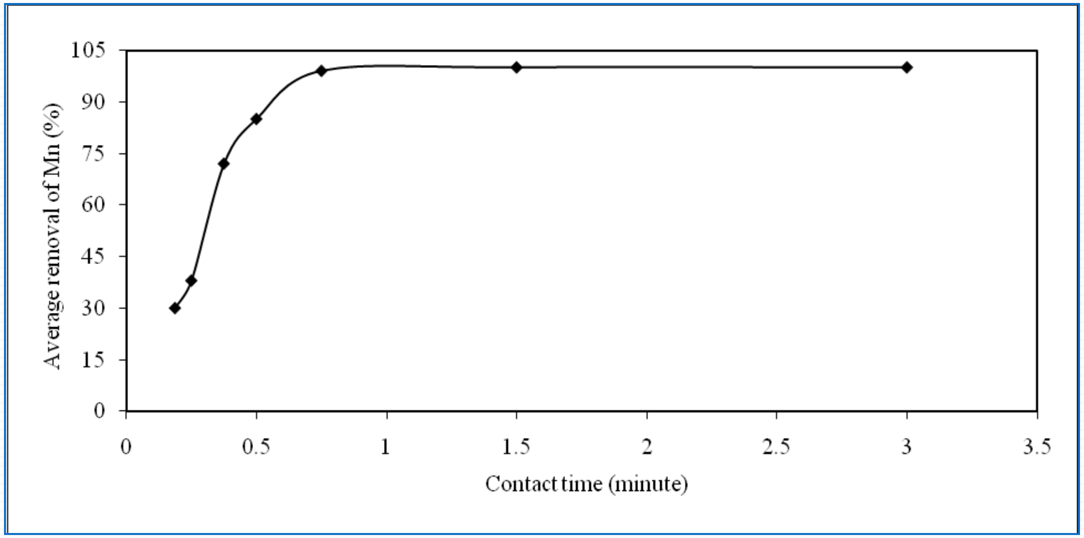



**Green sand**

# Removal of Mn: Effect of Flow Rate/ Contact Time

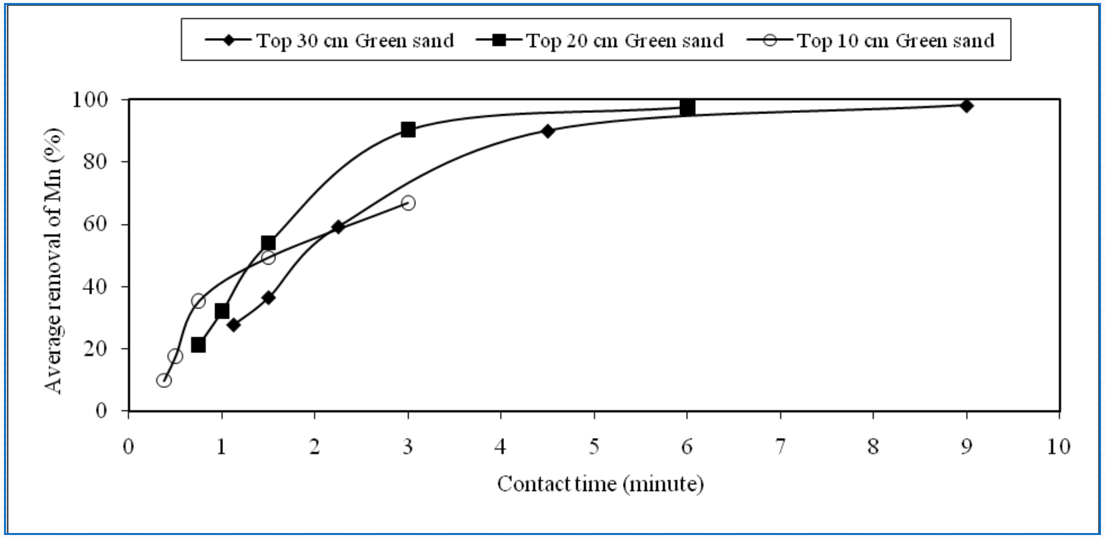



**Mn-coated sand**




**Synthetic Mn-coated sand**

# Removal of Mn: Effect of Flow Rate/ Contact Time




**Green sand**

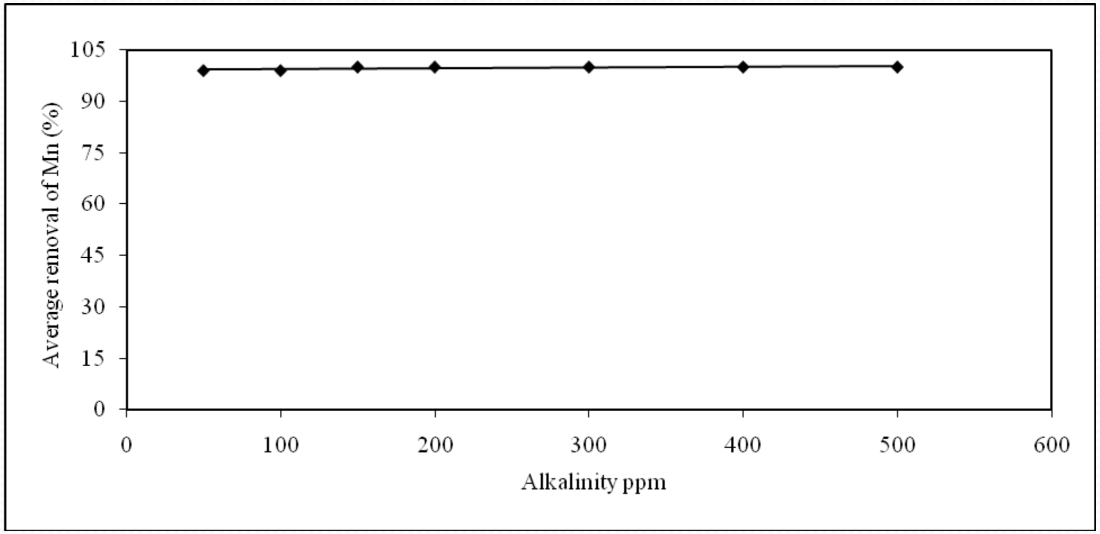
- Flow rate/ contact time has significant influence on Mn removal
- A contact time of about 1.5 – 3 minutes appear adequate for removal of Mn under the experimental conditions
- In all cases, Mn removal improved with increasing filter run time

# Removal of Mn: Effect of Initial Mn Concentration

| Initial Mn Concentration (mg/l) | Average Mn Removal (%) | | |
|---|---|---|---|
| | Mn-oxide coated sand (top 6 cm) | Synthetic Mn-coated sand (top 6cm) | Green Sand (top 20 cm) |
| 0.022 | 100 | 100 | 100 |
| 0.5 | 100 | 100 | 100 |
| 1.0 | 100 | 100 | 100 |
| 2.0 | 100 | 100 | 100 |
| 3.0 | 100 | 99 | 100 |
| 4.0 | 100 | 100 | 100 |
| 5.0 | 100 | 100 | 100 |

- If flow rate through the filter could be maintained at a low rate (in this case 1 ml/cm$^2$/min), then initial Mn concentration is not likely to affect the removal of Mn significantly.

# Removal of Mn: Effect of Alkalinity, Arsenic



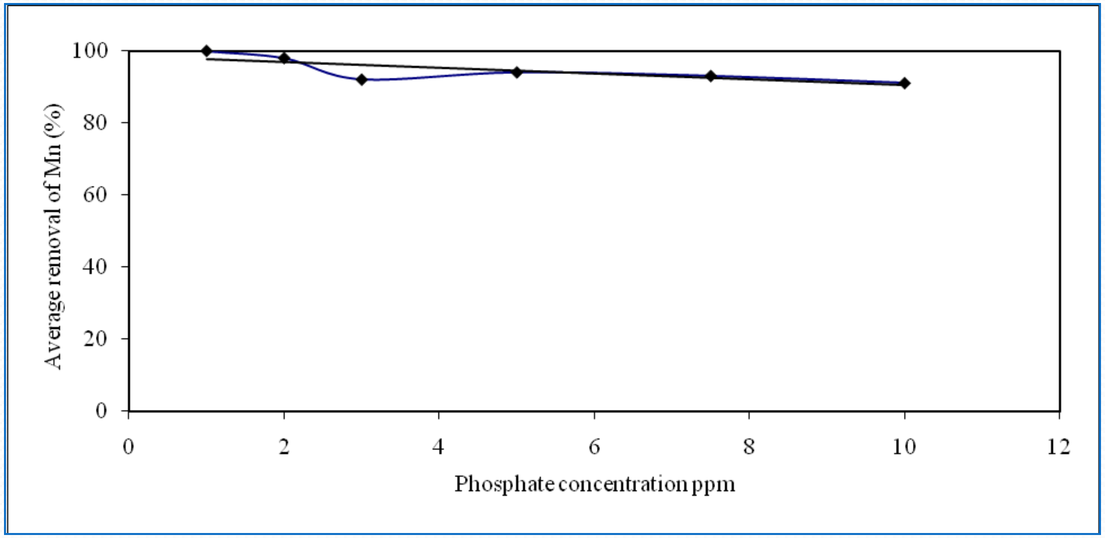

**Mn-coated sand column**

- Initial Mn = 2 mg/l
- Flow rate = 1 ml/cm$^2$/min

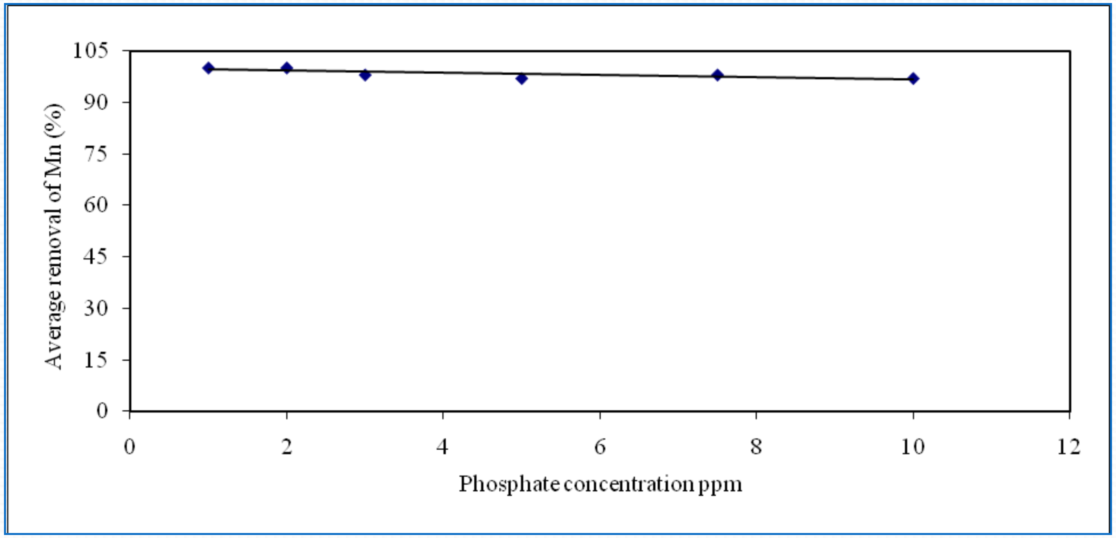
- Alkalinity (up to 500 mg/l) did not have any significant effect on removal of Mn in any of the three Mn-coated media.

- Similarly, presence of Arsenic (up to 500 μg/l) did not have any effect on Mn removal in any of the three Mn-coated media

# Removal of Mn: Effect of Phosphate



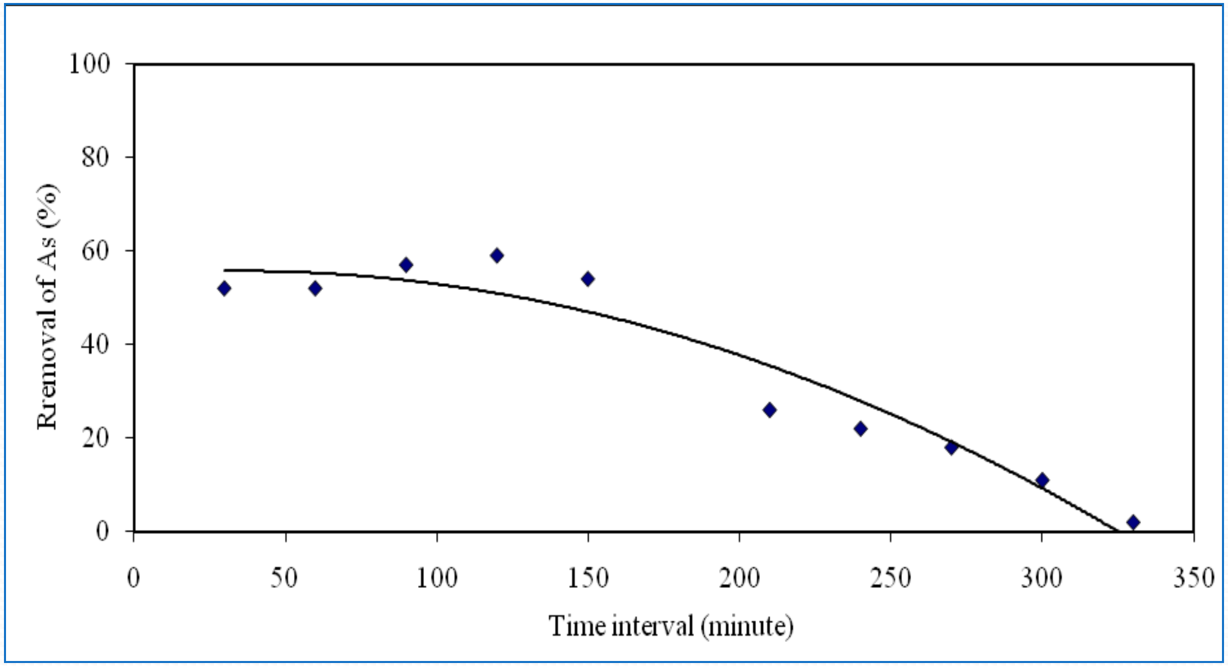

**Mn-coated sand**




**Green Sand**

Phosphate does not have significant impact on Mn-removal

# Removal of As: Effect of Filter Run Time

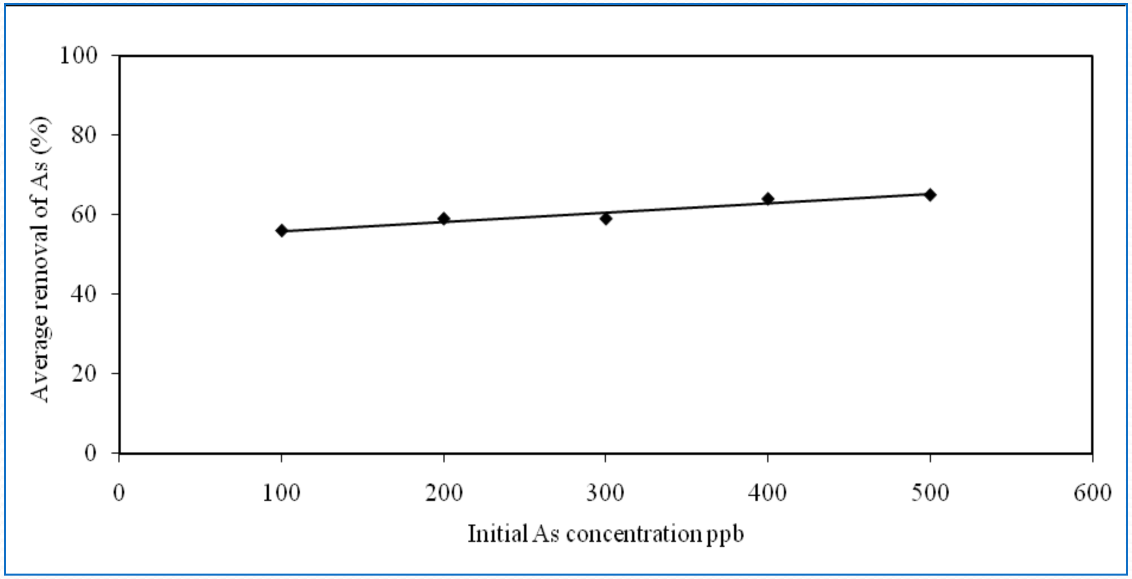



**Mn-coated sand column**

- **Initial As = 300 μg/l**
- **Flow rate = 1 ml/cm$^2$/min**

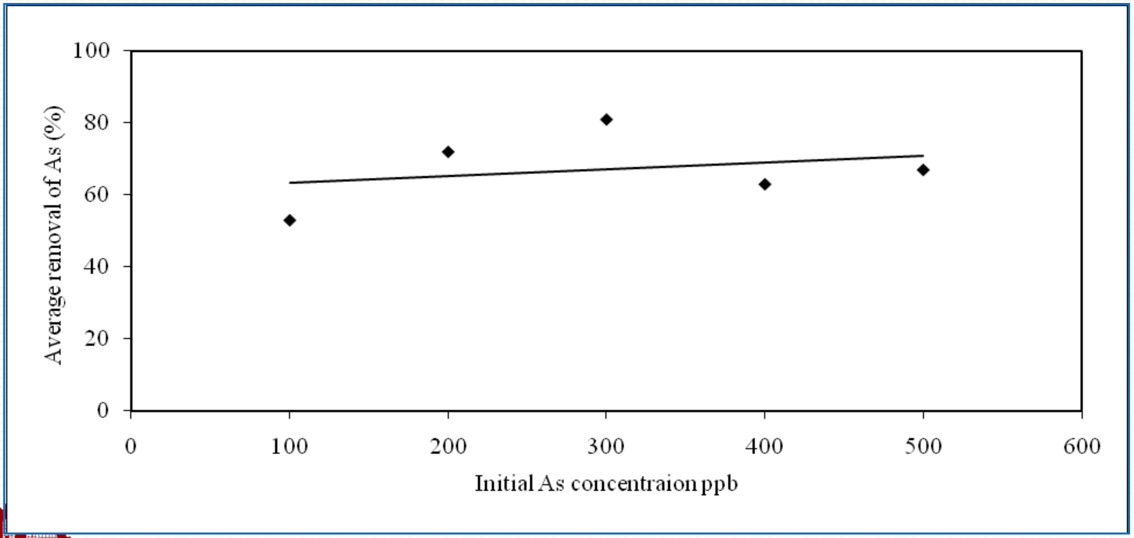
- Arsenic removal not significant
- Significant reduction of Arsenic removal with increasing filter run time

# Removal of As: Effect of Initial As Concentration




**Mn-coated sand**
(As removal up to 150 mins)

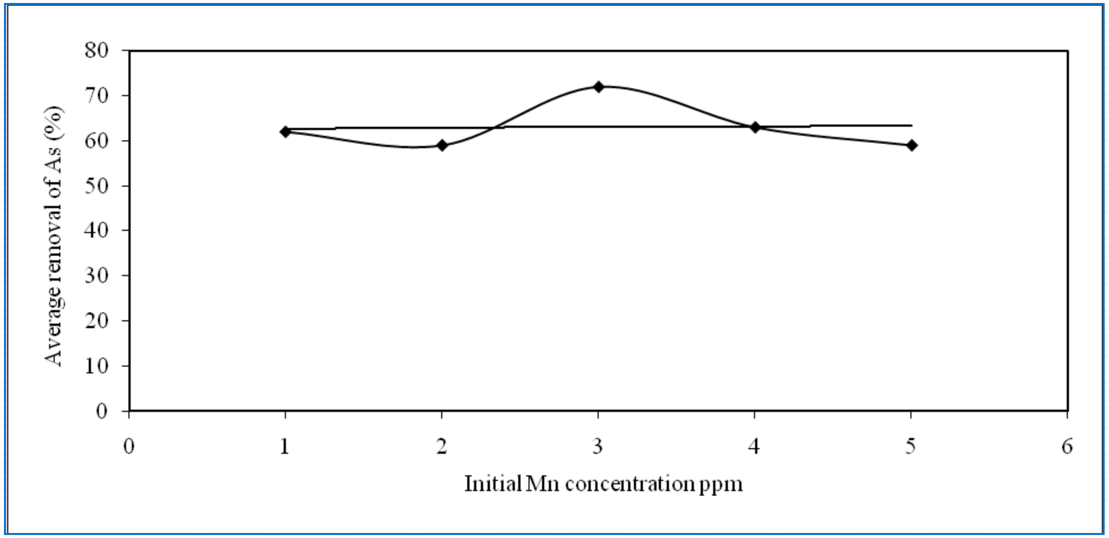
- **Initial As = 100-500 μg/l**
- **Flow rate = 1 ml/cm²/min**




**Green sand**
(As removal up to 150 mins)

Arsenic removal increases slightly with increasing initial As concentration

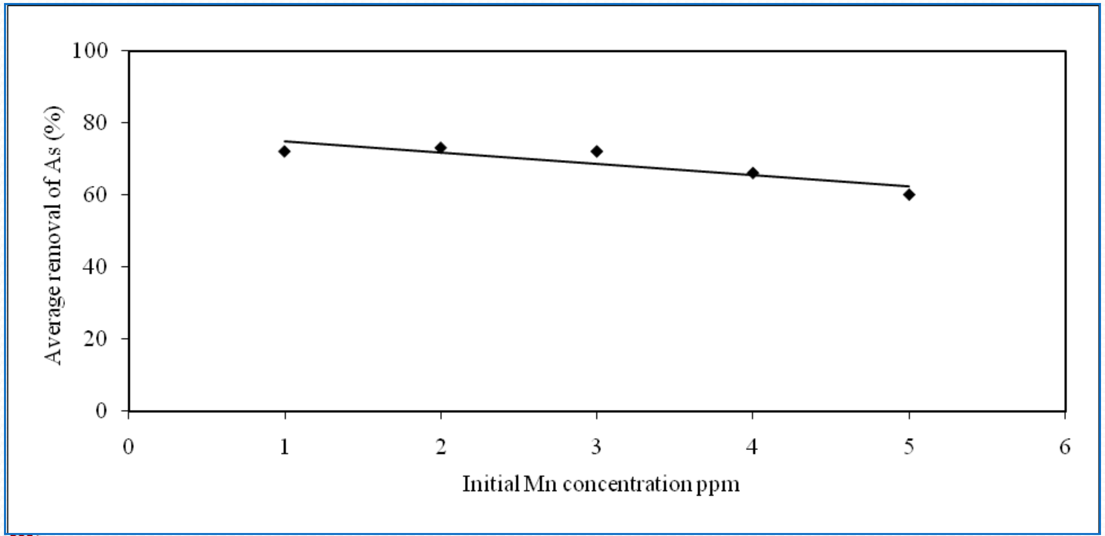
# *Removal of As: Effect of Mn*




**Mn-coated sand**

(As removal up to 150 mins)

- **Initial As = 300 μg/l**
- **Flow rate = 1 ml/cm²/min**

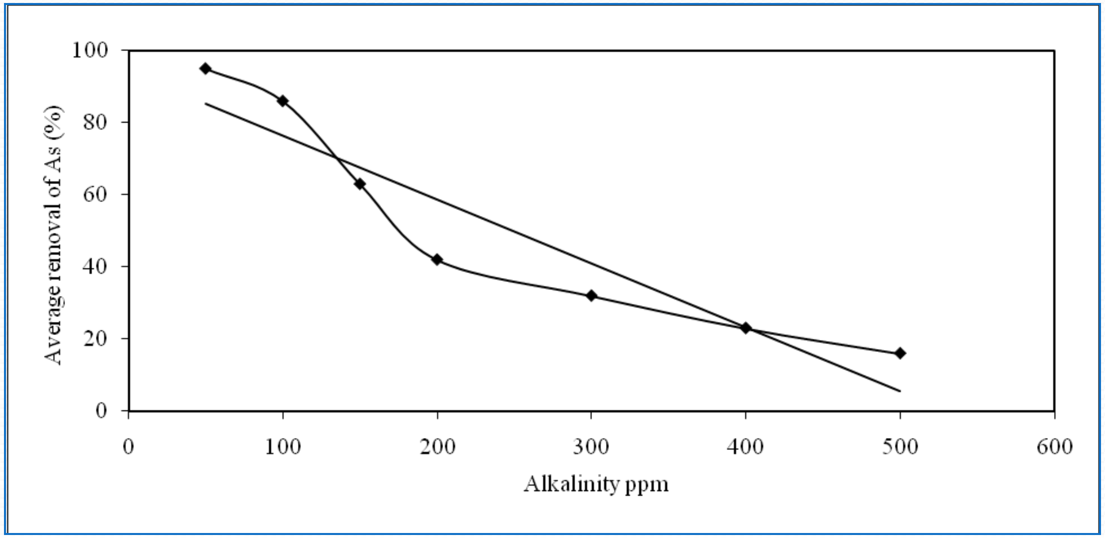



**Synthetic Mn-coated sand**

(As removal up to 150 mins)

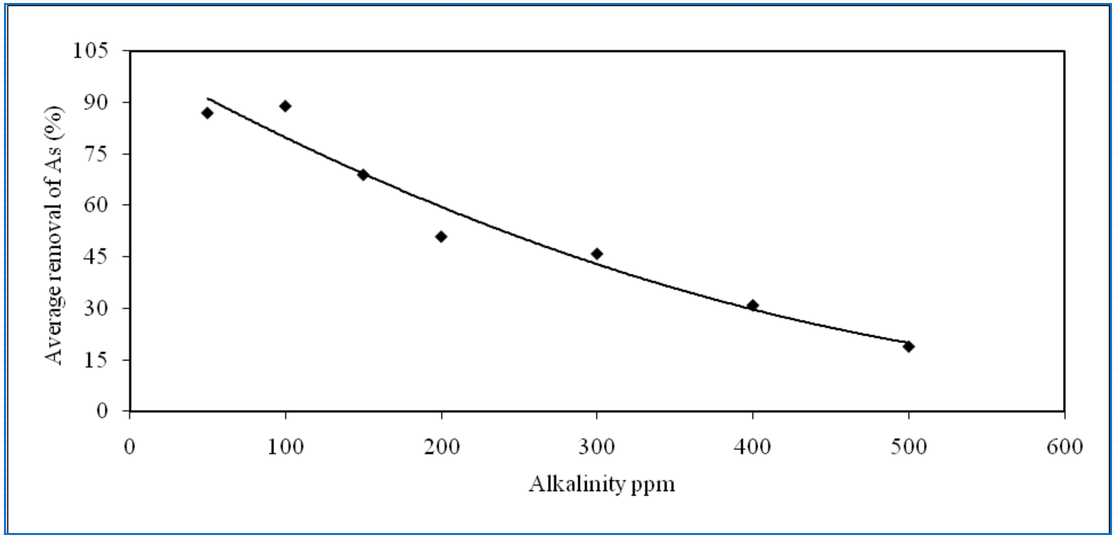
Arsenic removal not significantly affected by the presence of Manganese

# *Removal of As: Effect of Alkalinity*



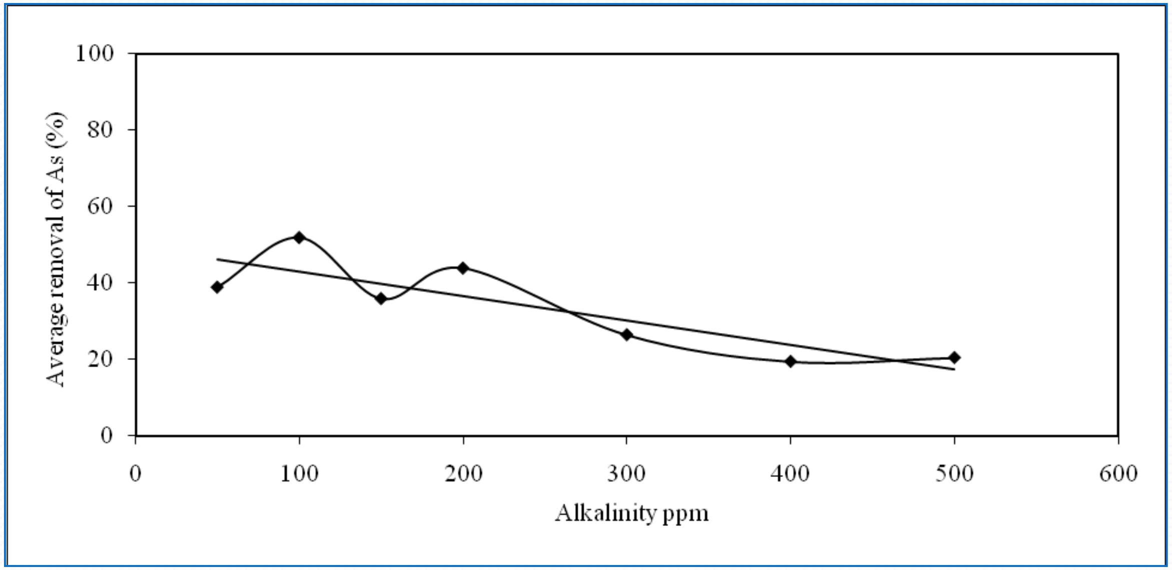

**Mn-coated sand**

- **Initial As = 300 μg/l**
- **Flow rate = 1 ml/cm$^2$/min**




**Synthetic Mn-coated sand**

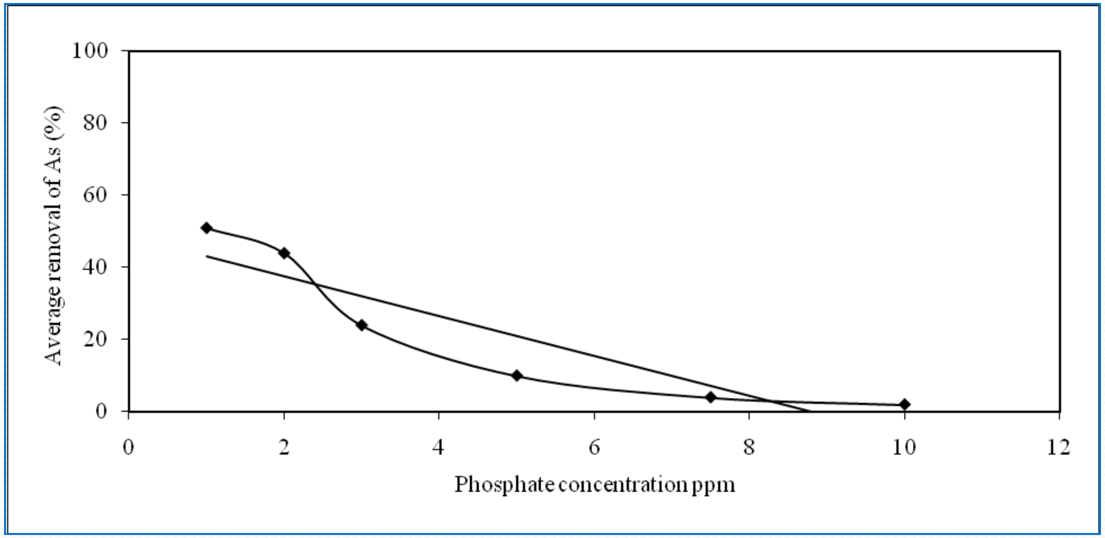
# Removal of As: Effect of Alkalinity




**Green sand**

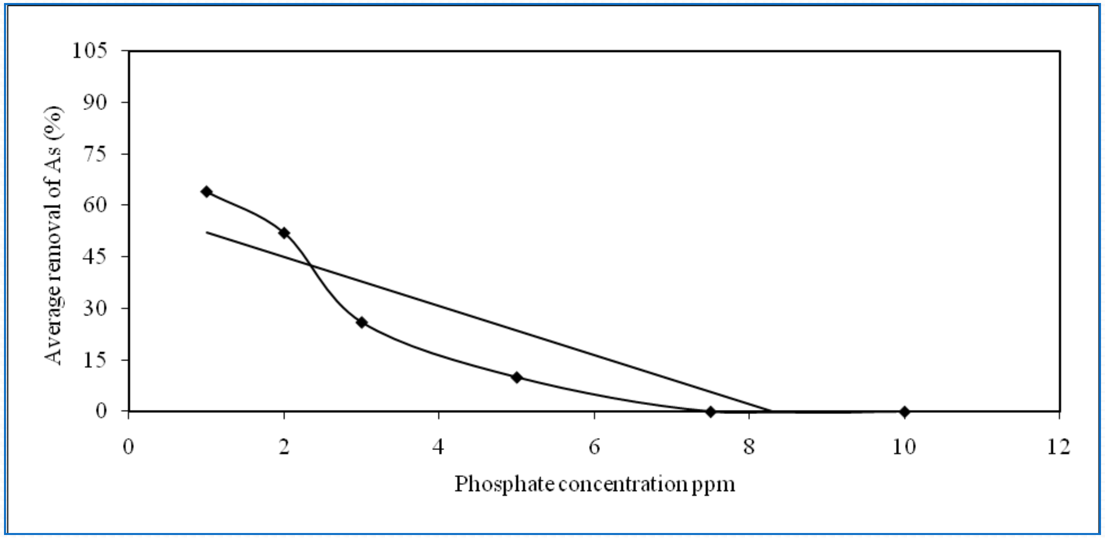
- Significant reduction of Arsenic removal with increasing Alkalinity
- Bicarbonate ion appears to compete strongly with Arsenic for adsorption on Mn-coated filter media

# Removal of As: Effect of Phosphate



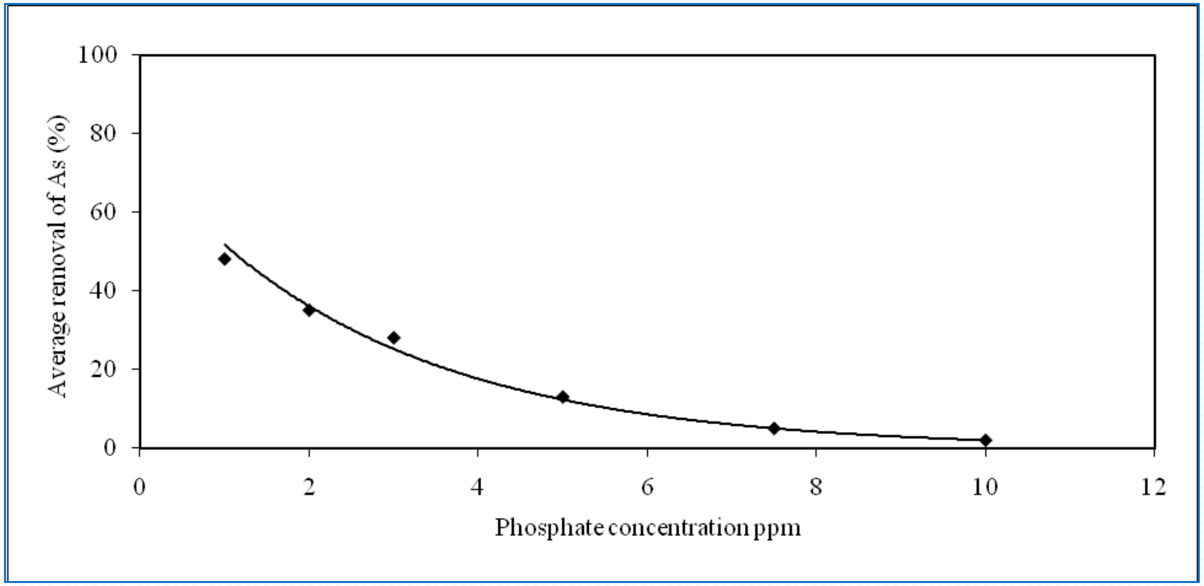

**Mn-coated sand**

- Initial As = 300 $\mu g/l$
- Flow rate = 1 $ml/cm^2/min$




**Synthetic Mn-coated sand**

# *Removal of As: Effect of Phosphate*




**Green sand**

- Significant reduction of Arsenic removal with increasing phosphate concentration; almost no As removal at phosphate concentration of 10 mg/l
- Phosphate ions compete strongly with Arsenic for adsorption on Mn-coated filter media

## *Evaluation of Selected Existing AIRPs*

- The As and Mn removal performance of 7 community groundwater treatment plants Manikganj and Sirajganj have been assessed.
- 5 community treatment plants (SEDA-IRPs) in Manikganj have been designed for removal of both Arsenic and Iron.
- 2 community treatment plants (ITN-BUET MSF) in Sirajganj have been designed as Fe-As-Mn removal plants

# SEDA-IRPs: Two Types

- Three plants (Plant No. M1, M4 and M5) consist of 3 chambers – aeration, filtration and storage chamber.

**3-Chamber SEDA Plant**

# *SEDA-IRPs: Two Types*

- The other two plants (Plant No. M2 and M3) consist of two chambers – aeration chamber and filtration chamber


**2-Chamber SEDA Plant**

# ITN-BUET-MSFs

- Consist of 3 chambers – aeration chamber, up-flow filter and down-flow filter

## *Sampling Schedule*

<table>
<tr><th>Location</th><th>Plant Identification No.</th><th>Installation Date</th><th>Sample Collection Dates</th></tr>
<tr><td>Manikganj</td><td>SEDA M1</td><td>05/11/2007</td><td rowspan="5">10/02/2010<br>09/03/2010<br>16/04/2010<br>13/05/2010<br>08/06/2010<br>08/07/2010<br>06/10/2010</td></tr>
<tr><td>Manikganj</td><td>SEDA M2</td><td>05/01/2004</td></tr>
<tr><td>Manikganj</td><td>SEDA M3</td><td>10/02/2009</td></tr>
<tr><td>Manikganj</td><td>SEDA M4</td><td>10/04/2001</td></tr>
<tr><td>Manikganj</td><td>SEDA M5</td><td>10/01/2010</td></tr>
<tr><td>Sirajganj</td><td>ITN-BUET S1</td><td>03/06/2008</td><td rowspan="2">26/02/2010<br>04/04/2010<br>06/05/2010<br>04/06/2010<br>09/07/2010<br>05/10/2010</td></tr>
<tr><td>Sirajganj</td><td>ITN-BUET S2</td><td>28/04/2009</td></tr>
</table>

- Water samples were analyzed for pH, $CO_2$, As, Mn, Fe, Phosphate, Alkalinity, etc. Solid samples were analyzed for Mn-content (extraction with hydroxylamine hydrochloride)

# Performance of SEDA Plants

## Iron (Fe) Removal:

- Fe of raw water varied form 7 to 13 mg/l.
- All 5 plants found to be very efficient in removing Fe
- Aeration followed by up-flow filtration found to be effective in removing Fe from groundwater

# Performance of SEDA Plants

## Arsenic (As) Removal:

- Raw water As in M5: 604 μg/l; M1-M4 : 60 to 120 μg/l.
- In M1-M4, As was removed to levels below Bangladesh standard. Removal efficiency varied, possibly due to degree of aeration achieved.
- Significant As was removed in the M5 plant (up to 88%), but because of high initial As (over 600 μg/l), treated water did not satisfy the Bangladesh standard.
- Raw water Fe concentration and effectiveness of aeration are principal factors determining As removal in SEDA plants.

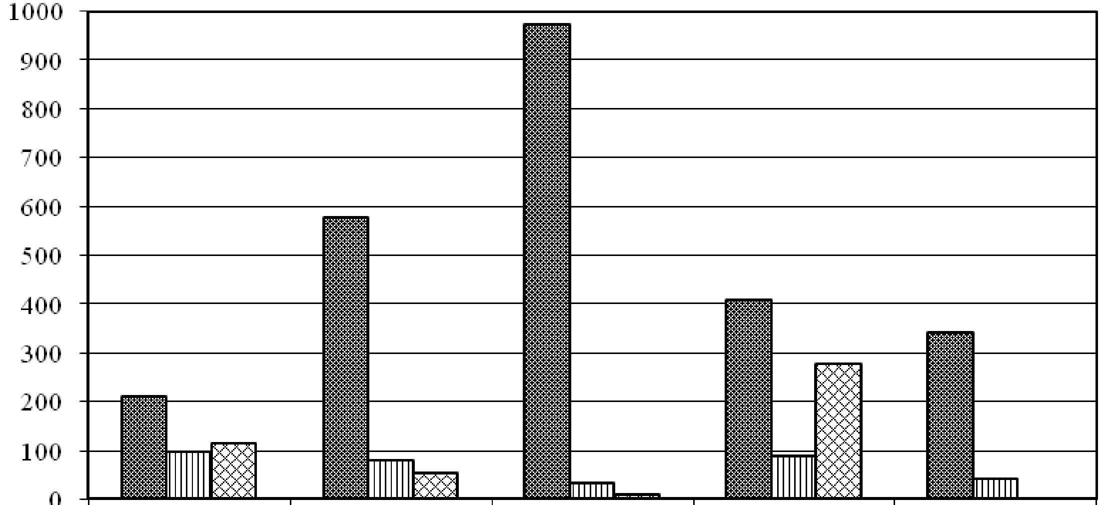
# Performance of SEDA Plants

## Manganese (Mn) Removal:

- Mn removal varied not only from plant to plant, but also varied with time for a particular plant

| ID | R/T | Sampling Date | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | 10/02/10 | 09/03/10 | 16/04/10 | 13/05/10 | 08/06/10 | 08/07/10 | 06/10/10 |
| M1 (2007) | R | 0.157 | 0.213 | 0.213 | 0.213 | 0.213 | 0.213 | 0.313 |
| | T | 0.004 | 0.005 | 0.080 | 0.003 | < 0.001 | < 0.001 | 0.222 |
| M2 (2004) | R | 0.716 | 0.579 | 0.579 | 0.579 | 0.579 | 0.579 | 0.668 |
| | T | 0.235 | 0.116 | 0.077 | 0.141 | < 0.001 | -- | 0.290 |
| M3 (2009) | R | 1.163 | 0.974 | 0.974 | 0.974 | 0.974 | 0.974 | 1.112 |
| | T | 0.914 | 0.648 | 0.439 | 0.182 | 0.630 | 0.850 | 0.721 |
| M4 (2001) | R | 0.329 | 0.409 | 0.409 | 0.409 | 0.409 | 0.409 | 0.580 |
| | T | 0.038 | 0.042 | 0.175 | 0.186 | 0.116 | 0.179 | 0.128 |
| M5 (2010) | R | 0.339 | 0.344 | 0.344 | 0.344 | 0.344 | 0.344 | 0.402 |
| | T | 0.146 | 0.193 | 0.084 | 0.027 | 0.168 | 0.005 | 0.144 |

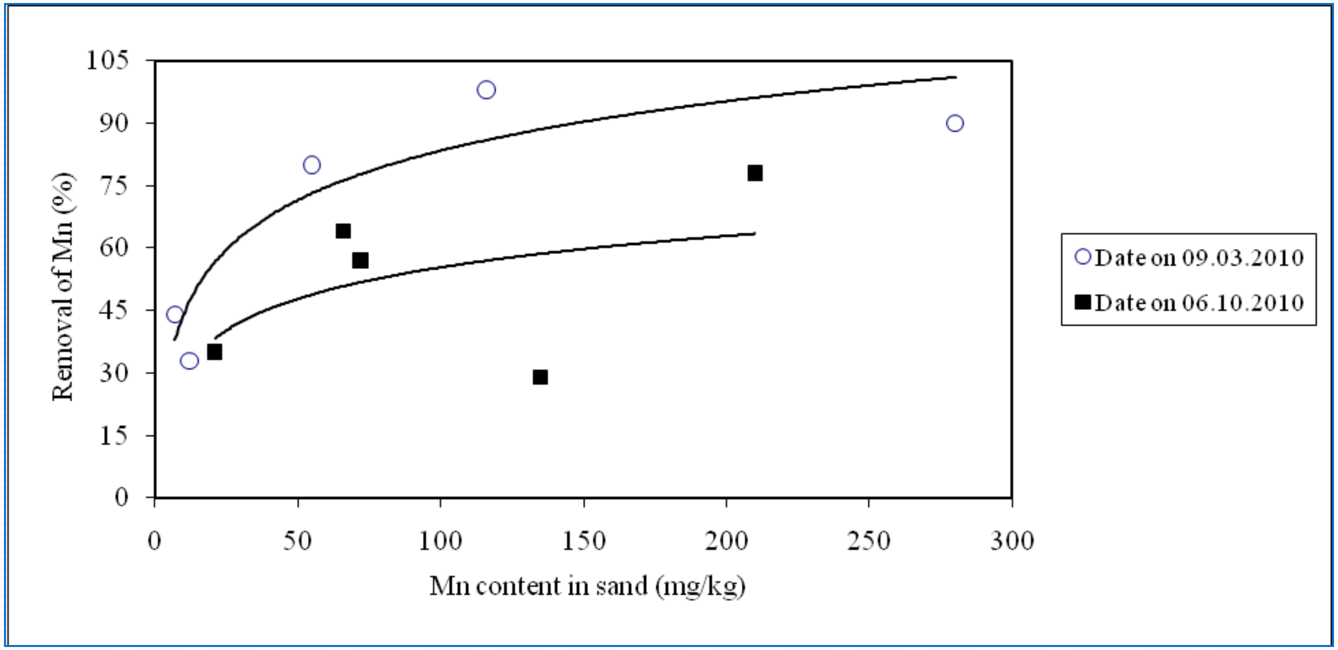
# Performance of SEDA Plants: Mn Removal




| | SEDA M1 | SEDA M2 | SEDA M3 | SEDA M4 | SEDA M5 |
|---|---|---|---|---|---|
| Mn con. ug/l | 213 | 579 | 974 | 409 | 344 |
| Removal of Mn % | 98 | 80 | 33 | 90 | 44 |
| Mn cont. of sand mg/kg | 116 | 55 | 12 | 280 | 7 |

- Mn removal and Mn-content of solids on 9 March 2010

# *Reasons for variable performalnce of SEDA plants in removing Mn*




- Mn-content of filter media is an important parameter; increasing Mn-content improved Mn removal efficiency.
  In general, Mn-content of filter media found to be low.

# *Reasons for variable performance of SEDA plants in removing Mn: Formation of Mn-coating*

- Mn content of the filter media in SEDA plants appear to depend mainly on filter run time and media washing practices (not so much on Mn content of raw water).

- Highest Mn content found in M4 (installed 2001). Mn content relatively lower for M3 (2009) and M5 (2010). Thus, it takes a long time for the formation on Mn-coating on filter media under field conditions.

- Filter media of M2 and M3 are washed frequently (once every 15 days). This washing practice probably also contributed to relatively low Mn content of media. One the other hand, the media of the M5 plant were not washed during the assessment period, and Mn content of media increased quickly from 7 mg/kg in March to 66 mg/kg in October.

# *Reasons for variable performance of SEDA plants in removing Mn: Effect of Washing*

- Filter media washing appear to significantly affect Mn removal performance. For example, M1 performed well during first 6 samplings, but performance deteriorated during 7$^{th}$ sampling in October 2010. Media of M1 plant was washed sometime in September 2010. The poor performance of M1 in October appears to be related to the washing of filter media.

- The poor performance of M2 and M3 plants and low Mn-content of media in M2 (compared to M1, which was installed later) could also be related to frequent washing of media of these two units.

- The relatively poor performance of M4 during April to October 2010 could also be related to the washing of the media of this plant in early April 2010.

# Performance of ITN-BUET MSFs

## Iron (Fe) Removal:

- Fe of raw water 13.2 and 34.2 mg/l
- Both plants found to be very efficient in removing Fe; majority of Fe removed in up-flow chamber
- Aeration followed by up-flow filtration found to be effective in removing Fe from groundwater

# Performance of ITN-BUET MSFs

## Arsenic (As) Removal:

- As of raw water 92 and 35 μg/l
- Both plants found to be efficient in removing As; majority of As removed in up-flow chamber along with Fe
- Raw water Fe concentration and effectiveness of aeration are principal factors determining As removal.

# Performance of ITN-BUET MSFs

## Manganese (Mn) Removal:

- Mn removal varied not only from plant to plant, but also varied with time for a particular plant

| Plant ID | Sample ID | Sampling Date | | | | | |
|---|---|---|---|---|---|---|---|
| | | 26/02/10 | 04/04/10 | 06/05/10 | 04/06/10 | 09/07/10 | 05/10/10 |
| S1 | Raw | 0.672 | 0.570 | 0.566 | 0.552 | 0.492 | 0.649 |
| | After U/F | 0.222 | -- | 0.120 | < 0.001 | 0.088 | 0.075 |
| | After D/F | 0.036 | 0.046 | 0.120 | < 0.001 | < 0.001 | < 0.001 |
| S2 | Raw | 1.646 | 1.526 | 1.411 | 1.537 | 1.476 | 1.609 |
| | After U/F | 1.303 | -- | 0.609 | 1.461 | 0.526 | 0.278 |
| | After D/F | 1.048 | 1.011 | 0.041 | < 0.001 | < 0.001 | < 0.001 |

# Performance of ITN-BUET MSFs

**Manganese (Mn) Removal:**

- In S1, significant Mn removal during 5 out of 6 samplings; majority of Mn removed in the up-flow filtration chamber.

- In S2, Mn removal very poor during first two samplings; Mn removal very good during last four samplings. Poor Mn removal in up-flow filtration chamber; down-flow chamber found more effective in removing Mn.

# *Variable performance of ITN-BUET MSFs in removing Mn: Media Mn-content and Flow rate*

- Manganese content of filter media is an important parameter for Mn removal. However, flow rate was also found to be very important in Mn removal; as found in laboratory experiments, higher flow rates resulted in poor Mn removal.

- Relatively better performance of S1 appears to be related to higher Mn-content of up-flow filter media and relatively slow filtration rate.

- Poor performance of S2 during first two samplings appears to be related to low Mn-content of the up-flow filter (also the down-flow filter), and relatively faster flow rate of water; relatively better performance of S2 during subsequent 4 samplings appears to be due to long residence time/ contact time of water in/ with filter media.

# PRELIMINARY DESIGN CRITERIA

# *Preliminary Design Criteria for Fe-As-Mn Removal in Community Groundwater Treatment Plant*

1. A treatment plant for simultaneous removal of Fe, As and Mn should consist of three chambers – Aeration Chamber, Up-flow filter Chamber, and Down-flow filter Chamber.

- The first Chamber to be designed for aeration/ oxidation of Fe(II) to Fe(III) [and possibly of some As(III) to As(V)] and subsequent precipitation of Fe(III) hydroxides. Adsorption of As onto Fe(III) hydroxides and co-precipitation of As with Fe(III) hydroxides will also take place in this Chamber.

- The Up-flow filter Chamber to be designed for continued oxidation of Fe(II) and adsorption/ co-precipitation of As, and retention of Fe(III) hydroxides flocs. Majority of Fe and As are likely to be removed in this up-flow Chamber. The current design practices (e.g., those used in the ITN-BUET MSF design) may be followed for the design of aeration chamber and up-flow filter.

## *Design Criteria for Optimal Removal of Fe-As-Mn in Community Groundwater Treatment Plant*

2. The Down-flow filtration Chamber should be designed primarily for removal of Mn, and for removal of the portion of Fe and As that escapes the Up-flow filter.

- Down-flow filter media should have a layer of Mn-oxide coated media (e.g., prepared/synthetic Mn-coated sand or Green sand) at the top; a Mn-content of 7000 mg/kg and above should perform well.

3. Depth of the Mn-oxide coated sand media should be such that the contact time with this media is greater than about 1.5 minutes.

4. The bottom of the Down-flow filter should consist of natural sand; the depth of this layer should be governed by the surface area of the filter and water storage requirements.

# *Design Criteria for Optimal Removal of Fe-As-Mn in Community Groundwater Treatment Plant*

5. Mn-oxide coated sand media at the top of Down-flow filter should not be disturbed or mixed with rest of the filter media during washing/ backwashing. Therefore, it is proposed that Mn-oxide coated media is placed separately, e.g., on a perforated tray at the top of the Down-flow filter.

6. Flow rate through the filter media (especially in the Down-flow Chamber) should be as low as practicable; a flow rate of about 1 $ml/cm^2/min$ appears adequate. Slower flow rates would also improve removal of Fe and As.

# *Concluding Remarks*

- It appears that it would be possible to design community treatment plants for effective simultaneous removal of Fe, As and Mn..
- It is important to design treatment plants for simultaneous removal of Fe, As and Mn, based on the preliminary design criteria proposed and to construct and operate such plants in the field.
- This is needed for finalization of design parameters and also for developing proper operation and maintenance guidelines for such plants.

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