



# Removal of Arsenic with Oyster Shell: Experimental Measurements

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## Abstract

Oyster shell has tremendous potential as a remediation material for the removal of arsenic from groundwater. A single arsenic removal system was developed with oyster shell for tube well water containing arsenic. The system removes arsenic from water by adsorption through fine oyster shell. Various conditions that affect the adsorption/desorption of arsenic were investigated. Adsorption column methods showed the removal of As(III) under the following conditions: initial As concentration, 100  $\mu\text{g/L}$ ; oyster shell amount, 6 g; particle size,  $<355\mu\text{m}$ ; treatment flow rate, 1.7 mL/min; and pH 6.5. Arsenic concentration of the treated water were below the Bangladesh drinking water standard of 50  $\mu\text{g/L}$  for As. The desorption efficiencies with 2M of KOH after the treatment of groundwater were in the range of 80-83%. A combination of techniques was used to measure the pH, conductivity, cations and anions. The average concentrations of other inorganic constituents of health concern (Na, K, Ca, Mg and Fe) in treated water were below their respective WHO guideline for drinking. The present study might provide new avenues to achieve the arsenic concentrations required for drinking water recommended by Bangladesh and the World Health Organization (WHO).

**Keywords:** arsenic, removal, oyster shell, adsorption, speciation.

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## Introduction

Arsenic is widely distributed in the environment. Natural processes including soil erosion, mineral leaching and weathering are responsible for introducing arsenic into surface waters [1]. Arsenic enriched geothermal waters can also significantly contribute to increase amounts of arsenic in surface waters [2]. Industrial activities, such as mining and smelting of metal ores, combustion of fossil fuels, use of arsenical pesticides and waste effluents from manufacturing have resulted in the contamination of air, soils, and surface waters by arsenic compounds [3]. Arsenic occurs as organic and inorganic compounds in natural waters. Inorganic arsenic compounds are arsenolite ( $\text{As}_2\text{O}_3$ ), arsenic oxide ( $\text{As}_2\text{O}_5$ ) or realgar ( $\text{As}_2\text{S}_2$ ), resulted from dissolution of minerals. Arsenic used to be present in two forms: arsenate As (V) or arsenite As (III). Arsenic content in a solution depends on pH and redox potential. Arsenates are thermodynamically stable forms of inorganic particles, dominant in surface waters. Arsenites exist under reduction conditions, in anaerobic underground waters. It is found that arsenic toxicity

depends on the degree of its oxidation. Arsenites are more toxic three valent arsenic forms for biological systems as compared to arsenates. The toxicity of organic-arsenic compounds is lower as compared to inorganic forms of arsenic [4, 5].

Arsenic is one of the most important global environmental toxicants. High concentrations of arsenic in ground water have been reported from several countries, including Argentina, Bangladesh, Chile, China, India, Italy, Japan, Mexico, Malaysia, Monogolia, Nepal, Poland, Taiwan, Vietnam, and some parts of the United States [6-13]. The arsenic calamity of Bangladesh can be described as the largest known mass poisoning in the history, with an estimated 35–77 million people exposed to arsenic-contaminated drinking water [14]. Arsenic contamination has been reported in groundwater in 61 out of the 64 districts in Bangladesh. About 61% of the tube wells have arsenic content above 0.05 mg/L and about 13% have arsenic content above 10 $\mu\text{g/L}$  [15]. This is significantly higher

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than the World Health Organization (WHO) maximum permissible limit in drinking water (50 µg/L) and the recommended value is 10 µg/L [16]. The Environmental Protection Agency (EPA) has recently adjusted the upper limit, 10 µg/L [17], for arsenic in drinking water. Due to its high toxicity, standard for arsenic in drinking water has become more stringent. In Australia, the drinking water standard limit of As is set at only 7 µg/L while 50 µg/L is applied in other countries such as Bangladesh, India.

Arsenic can be removed from aqueous solution by using many technologies such as ion exchange resin, activated alumina, coprecipitation with iron or alum, reverse osmosis, membrane filtration, modified coagulation/filtration, and enhanced lime softening [18-22]. However, none of these technologies are currently applied on a broad scale in developing countries like Bangladesh because they require sophisticated technical systems and are therefore unpractical in low income regions. Among these methods, the adsorption techniques are simple and convenient, and have the potential for regeneration and sludge free operation. So far, various adsorbents for arsenic removal have been developed that include such materials as metal-loaded coral limestone, hematite and feldspar, activated carbon, activated alumina and hydrous zirconium oxide. However, most of these adsorbents entail several problems in terms of efficiency and cost. Bangladesh is a riverine country. D. Tsiamis studied the removal of As(III) with clam shells [23]. However, about 70% As(III) could be removed using clam shell. There are many canals, ponds all over the country. These are the living place of oysters. Therefore, the oyster shells are readily available to the people of Bangladesh. Thus oyster shell would become a promising simple adsorbent for the removal of arsenic.

The present work was performed to evaluate the use of waste oyster shell without any chemical pretreatment as an alternate adsorbent for removing As(III) from aqueous medium. Moreover, the oyster shell was applied for the removal of arsenic from As-contaminated drinking water samples in a single-step column operation.

## Materials and Methods

### Reagent

All reagents used throughout this work were of analytical-grade purity. Arsenic (III) standard solution (1000 mg/L) was procured from Aldrich Company and NaOH, KOH, HCl, HNO<sub>3</sub>, and H<sub>2</sub>SO<sub>4</sub> were obtained from Merck, Germany. Stock solutions (100 µg/L) of As(III) was prepared in de-ionized water from Arsenic(III) standard solution of 1000 mg/L. Dilute

standard solutions of arsenic were freshly prepared before use.

### Preparation of adsorbents

The oyster shell used in the present work was obtained from a local poultry shop which contained mostly calcium 295 mg/Kg, magnesium 78.8 mg/Kg, phosphorus 150 mg/Kg, iron 420 mg/Kg, copper 7 mg/Kg, zinc 5 mg/Kg and aluminium 4 mg/Kg (by Atomic Absorption and UV-Visible Spectrophotometric method). Moreover, the price of oyster shell was very low. The collected shells were washed with pure water several times to remove dust and fines. The washed materials were then dried in a hot-air oven at 60°C for 24 hour. The washed dried materials were grinded and sieved into the following three size fractions (600-425 µm, (425-355) µm and <355 µm. These materials were used for the removal of arsenic without further chemical treatment.

### Adsorption and Analytical Procedures

Oyster shell (2.0-8.0) g was added to the treatment glass column dimension (i.d 2.0 cm x 30.0 cm). The adsorption experiments were carried out in columns that were equipped with a stopper for controlling the column elution flow rate (treatment rate). Adsorption factors including the amount of oyster shell (2.0-8.0)g, particle size (<355-600) µm, treatment flow rate (1.7-6.7) mL/min, initial sample concentration (50-500) µg/L, and pH (2-14) were evaluated. After the adjustment of pH to the desired value with HCl and NaOH solutions, the sample solution (100 mL) was passed through the adsorption column at a given flow rate. The packing density of the treatment column was 0.50 g/cm<sup>3</sup> of dry oyster shell (particle size: <355 µm). A small piece of glass wool was inserted into the bottom of the column to prevent the loss of oyster shell during the treatment. The flow rate was kept constant by controlling the stopper valve. The removal (adsorption) efficiency was calculated using the following equation:

$$\text{Removal (adsorption) efficiency} = (C_0 - C_e) / C_0 \times 100 \quad (1)$$

Where, C<sub>0</sub> and C<sub>e</sub> are the concentration of As in the sample solution before treatment and after treatment, respectively.

### Analysis of Arsenic

The treated and non treated sample solutions were analyzed using the Hydride Vapor Generator (HVG) attached with Atomic Absorption Spectrometer (AAS-680, Shimadzu, Japan) for the determination of total arsenic followed by the generation of arsine gas

(AsH<sub>3</sub>). All reagents and chemicals were of analytical grade. Preparations of reagents were made with distilled deionized water.

#### **Sodium borohydride solution (0.5% NaBH<sub>4</sub>)**

3.0 g of sodium hydroxide & 2.5g of sodium borohydride (both were analer grade) were dissolved in distilled deionized water and then water was added to make the solution 500ml.

#### **Hydrochloric acid solution**

Concentrated hydrochloric acid (35-37% and analytical grade) was diluted to make 500ml of 5M HCl.

#### **Preparation of standard arsenic solution**

Arsenic standard solution of 1000 ppm was supplied. 1.0ml from 1000 ppm standard arsenic solution was taken in 100 ml volumetric flask to prepare 10ppm solution with deionized water. Again 10 ml from 10 ppm was pipetted in 100ml volumetric flask to prepare 1000 ppb solution. Then 0.1ml, 0.2ml, 0.3ml, 0.4ml and 0.5ml had been taken from 1000 ppb solution in five 100ml volumetric flasks to prepare 1ppb, 2 ppb, 3 ppb, 4 ppb and 5 ppb solution. Then 0.2ml conc. HCl (35-37%) and 2.0g KI were added in each solution and then made up to the mark with deionized water. The solutions were left for two hours.

#### **HVG-AAS Analysis Conditions.**

| Instrument condition       | Measurement condition         | Flame condition                                   |
|----------------------------|-------------------------------|---|
| Mode: Hollow cathode       | Signal process: Integral Hold | Fuel flow: 2.2L /min                              |
| Current: 8mA               | Integration time: 10sec       | Acetylene pressure: 0.9bar                        |
| Slit: 0.6nm                | CV: 10%<br>Pre spray: 3       | N <sub>2</sub> (Carrier gas)<br>Pressure: 3.4 bar |
| Wave length of As: 193.7nm | Repeat: 2<br>Maximum: 3       | Fuel: air-acetylene                               |

The standard and samples were aspirated in the following sequences for the preparation of the calibration curve and measuring the concentration of arsenic in the samples respectively: Blank-Standard-Measurement of analyte samples. At low concentrations, there is a linear relationship between the absorbance and concentration, but at higher concentrations it is non-linear and large errors can be introduced. Therefore, for atomic absorption work, the best results are obtained from the linear range; often samples were diluted so that the Beer's law was obeyed

#### **Calibration curve**

A calibration curve in Atomic Absorption measurement was obtained by aspirating the standard solution into the flame; standard solution containing known concentration of the element to be determined and by measuring the absorption of each solution a graph was obtained.

#### **Analysis of Samples**

The treated samples were diluted to a known volume and 2.0g of KI and 2.0ml concentrated HCl were also added to each of the sample; then the samples were allowed to stand for two hours and after that samples were analyzed by HVG-AAS [24]. The samples were analyzed against a calibration curve prepared by standard solutions of arsenic. A reagent blank was also maintained and the absorption due to the blank reagent was subtracted. Each unknown samples were analyzed for three times.

#### **Analysis of Na, K, Ca, Mg and Fe**

Na, K, Ca, Mg and Fe were analyzed using Atomic Absorption Spectrophotometer (Model: AA-680, Shimadzu, Japan) [24]. Quality control measures for each element including calibration with reference samples, blanks and replicate analysis followed throughout the analysis in order to ensure reliable analytical data. Two blank samples were run with each set of samples to check the purity of the reagent and the possibility of contamination. Precision and analytical accuracy of the methods were evaluated by analyzing standard reference material, Wheat flour, SRM 8437 (National Institute of Standard and Technology, USA).

#### **Analysis of Cl<sup>-</sup>, PO<sub>4</sub><sup>3-</sup> and SO<sub>4</sub><sup>2-</sup>**

Cl<sup>-</sup>, PO<sub>4</sub><sup>3-</sup> and SO<sub>4</sub><sup>2-</sup> from the treated and non treated samples were analyzed by UV-Visible Spectrophotometric method [24].

#### **Results and Discussion**

The performances of oyster shell were evaluated for the removal of As (III). Preliminary studies showed that the removal of As(III) was achieved under the following conditions: initial concentration: 100µg/L; amount of oyster shell: 6.0 g; treatment flow rates 1.7 mL/min and particle size <355µm. The removal efficiencies for As(III) with rice straw, tea leaves, and newspaper were 65%, 57%, and 18%, respectively. These three adsorbents had lower removal efficiencies than oyster shell. Therefore, they were not considered for further investigations. The main

components of oyster shell are calcium carbonate and carbon-OH etc., and are to be used as an adsorbent. Oyster shell was chosen for use as an adsorbent material because it has potential component and are available all over Bangladesh.

### Effect of Adsorbent Amount

The effect of the amount of oyster shell on the removal of As (III) was investigated. Fig. 1, shows that about 93% of arsenic was removed with 6.0 g oyster shell. The removal efficiencies of As(III) increased gradually with increasing amount of oyster shell. The adsorption capacity of oyster shell depends on the surface activity, that is the specific surface area available for As-surface interactions which is accessible to the As(III). With increasing the amount of oyster shell (from 2.0g to 8.0g) removal efficiency also increased at relatively low treatment flow rates and particle size <355 $\mu\text{m}$ . However, 8.0 g of adsorbent also showed the similar removal efficiency with same particle size of <355 $\mu\text{m}$ . This was due to the agglomeration of the oyster shell particles themselves so that the removal efficiency was not increased with amount of adsorbents. Therefore 6.0 g of adsorbent was chosen for the next experiment.

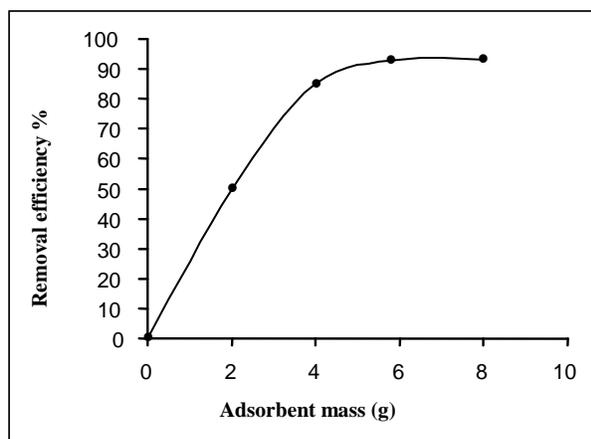


Figure 1. Effect of adsorbent amount on the removal of As(III) by adsorption onto oyster shell.

100  $\mu\text{g/L}$  input As concentration  
1.7 mL/min, flow rate  
Particle size: <355  $\mu\text{m}$   
pH 6.5  
100 mL, Volume used

### Effect of Particle Size

Column adsorption experiments were carried out for the removal of As(III) from aqueous solution

using three different particle sizes [<355 $\mu\text{m}$ , (355-425)  $\mu\text{m}$  and (425-600)  $\mu\text{m}$ ] with the constant amount of oyster shell. About 93% arsenic was removed by 6.0 g of oyster shell with the particle size of <355 $\mu\text{m}$  as shown in Fig. 2. From the Fig. 2, it is clear that lower the particle size higher the adsorption efficiency. The size of the oyster shell particles increased, the adsorption of metal ions decreased. These phenomena might be due to the fact that the smaller particles offer comparatively larger surface areas and greater numbers of adsorption sites. Therefore, particle size <355 $\mu\text{m}$  was chosen for the next experiment.

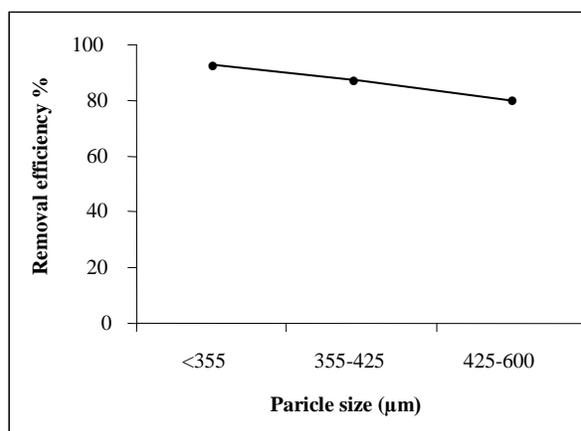
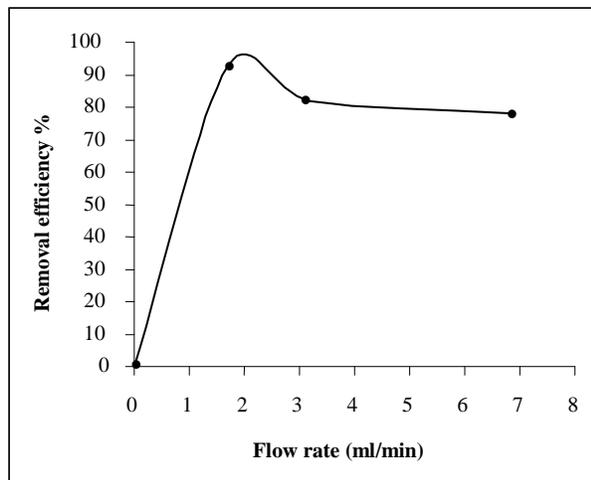


Figure 2. Effect of particle size for the removal of As(III) by adsorption onto oyster shell.

100  $\mu\text{g/L}$  input As concentration  
1.7 mL/min, flow rate  
Adsorbent mass: 6.0 g  
pH 6.5  
100 mL, Volume used

### Effect of Flow Rate

The effect of flow rate into column adsorption experiments was investigated for the removal of As(III). In Fig. 3, it is observed that the lower the flow rate (1.7 ml/min), the higher is the removal efficiency of As(III), where the particle size was <325 $\mu\text{m}$  and the amount of adsorbent was 6.0 g. These phenomena might be due to the fact that at the slower flow rate condition, arsenic in the solution got more contact time with the active surfaces of the oyster shell adsorbents. From this experiment, it is clear that highest removal efficiency could be achieved with lower treatment flow rate, lower particle size and higher amount of adsorbents. Therefore, 6.0 g of oyster shell, <325 $\mu\text{m}$  of particle size and 1.7 mL/min of flow rate were selected for the next experiment.

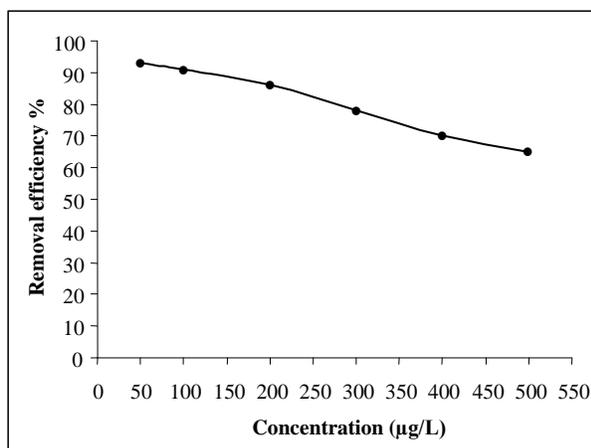


**Figure 3.** Effect of treatment flow rate on the removal of As(III) by adsorption onto oyster shell.

100 µg/L input As concentration  
 Particle size: <355 µm  
 Adsorbent mass: 6.0 g  
 pH 6.5  
 100 mL, Volume used

#### *Effect of Initial Concentration*

The removal efficiency is highly dependent on the initial concentrations of As (III) in the sample solution. The effect of the initial sample concentration on the removal of arsenic with oyster shell was investigated. The initial concentration was evaluated in the range of 50-500 µg/L and the results were illustrated in Fig. 4.



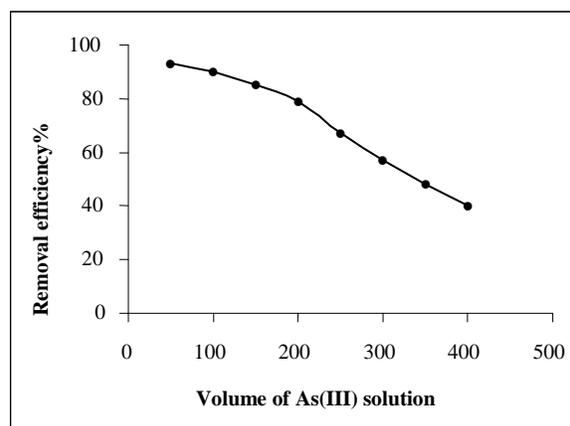
**Figure 4.** Effect of initial concentration of As(III) for the removal of As(III) by adsorption onto oyster shell.

100 µg/L input As concentration  
 Particle size: <355 µm  
 1.7 mL/min, flow rate  
 Adsorbent mass: 6.0 g  
 pH 6.5

The removal efficiency decreased with increasing of initial concentration of sample solution. From this experiment, it is observed that higher removal efficiency was achieved using 50µg/L of As(III) solution. These phenomena might due to the fact that at low concentration, most of the As(III) in the solution might contact with active sites of adsorbents. However, at higher concentration, most of the As(III) species were not able to contact with the active surfaces because the sites might have been occupied by the other arsenic (III) species present in the solution. The higher removal efficiency was achieved using 50µg/L of As(III) solution, however the WHO (World Health Organization) guideline value of arsenic in drinking water for Bangladesh is 50µg/L. Therefore, 100µg/L As(III) solution was chosen for the next experiment.

#### **Effect of the volume of As(III) solution**

As it is desired to obtain the optimum conditions for the development of a noble method for arsenic removal; the effect of initial volume was also investigated. Different initial volumes with optimized concentration 100 µg/ L As(III) solution were treated onto oyster shell and results were summarized in Fig. 5. It shows clearly that removal efficiency decreases with increase of initial volume. The removal efficiency varied from 93 to 40 % with initial volume 50 mL to 400 mL. This removal efficiency decreases probably due to the decreased of contact of arsenic with active sites on oyster shell. At lower volume of As(III) solution, most of arsenic might get available adsorbent sites. Moreover, increasing volume of the As(III) solution, active adsorbent sites were unavailable due to filled by the previous As(III).



**Figure 5.** Effect of initial volume of As(III) solution onto oyster shell.

Initial As concentration: 100 µg/L  
 Amount of oyster shell: 6.0 g  
 Particle size: <355 µm  
 Flow rate 1.7 ml/min  
 pH: 6.5

### Effect of pH

pH is one of the most important parameters controlling the metal ion sorption process [25,26]. Figure 6, showed the variation of removal efficiency of As(III) with pH of the solution. The maximum removal efficiency for As (III) was observed in comparatively neutral region at pH 6.5. This result should be of great advantage for the practical implementation of arsenic removal from groundwater. For the removal of As(III), the efficiency curve was essentially a pyramidal in the pH range 4-10, and then the efficiency tended to decrease with increasing of pH.

### Adsorption Mechanism

Arsenic removal by adsorption onto oyster shell can be supposed to occur mainly through two routes: (i) affinity adsorption and (ii) anion exchange between the arsenic in the water and the carbon surface of the oyster shell. pH is one of the most important parameters controlling the metal ion sorption process[25,26]. Fig. 5 depicts the effect of pH with the removal of arsenic by oyster shell. The poor As removal efficiencies at high pH can be attributed to the following factors: First, the chemical species of As(III) in this pH region are oxyanions. Next, hydroxyl groups are more plentiful on the surface of oyster shell with increasing of pH.

Affinity adsorption is related to the surface behavior of oyster shell, whereas anion exchange relates to the existing forms of the arsenic species. OH groups are created on the carbon surface during the activation process [27,28]. The mechanism of adsorption of metal anions onto activated carbon is generally well explained by electrochemical theory: Carbon in contact with water reduces oxygen to a hydroxyl group [29] and thus, the carbon loses electrons and become positively charged.



Electrical neutrality is maintained with hydroxyl ions, resulting in their adsorption. Although the oyster shell used in the present work was not subjected to any chemical or physical activation treatment, a large number of OH groups will remain on the surface of the oyster shell after the drying process. When a metal bearing solution contains anions that exhibit a higher affinity toward carbon than the hydroxyl groups, the latter are exchanged, as shown in the case of As (V)



At pH values of less than 9, neutral  $\text{H}_3\text{AsO}_3$  is predominantly present as As (III) species. These results

can be attributed to the lack of electrostatic repulsion between the surface and the neutral As(III) species. The physical adsorption and interaction between the  $\text{H}_3\text{AsO}_3$  species and the oyster surface might be partly responsible for the removal of As(III).

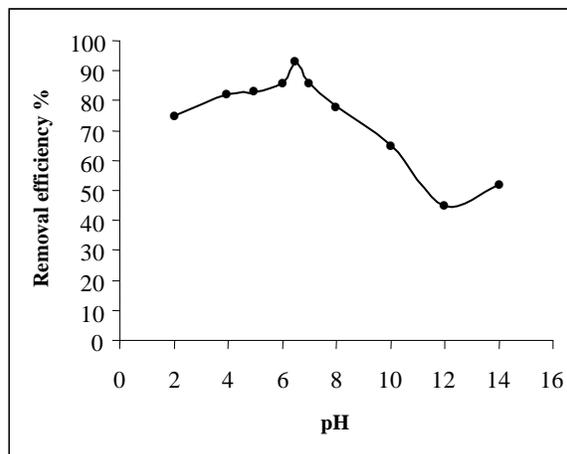


Figure 6. Effect of pH on the removal of As(III) by adsorption onto oyster shell.

Initial As concentration: 100  $\mu\text{g/L}$   
 Amount of oyster shell: 6.0 g  
 Particle size: <355  $\mu\text{m}$   
 100 mL, Volume used  
 Flow rate: 1.7 ml/min

### Desorption

Recovery of the adsorbed material and regeneration of the adsorbent are also important aspects of wastewater treatment. Attempts were made to desorb As(III) from the oyster shell surface with various eluents, such as hydrochloric, sulfuric, and nitric acid solutions and base solutions containing sodium hydroxide and potassium hydroxide. This desorption process was performed using the batch method. For each experiment, 50 mL of desorption solution was added to the column and held there for a fixed period of time. After the standing time, the solution was passed through the column. The results are presented in Table 1. Although the achievement of arsenic elution using strong acidic or alkaline solutions has been reported in the literature [30] the present work showed that effective desorption was obtained with alkaline solutions. Desorption of As (III) was very poor in the acidic media. During this experiment, the addition of acid into oyster shell causes a self degradation. As a result desorption efficiency was very poor in the acidic media. These phenomena are consistent with the results observed for the effect of pH. In general, the desorption efficiency of arsenic tended to increase with increasing desorption time. Consequently, potassium hydroxide solution was useful for desorption of arsenic from the surface of oyster shell.

**Table 1.** Influence of the Eluent on the Desorption of As(III)<sup>a</sup>.

| Desorption agent | Standing period (h) | Desorption (%) |
|------------------|---------------------|----------------|
| KOH (2M)         | 8                   | 68             |
|                  | 12                  | 68             |
|                  | 18                  | 71             |
|                  | 24                  | 77             |
|                  | 36                  | 83             |
| KOH (1M)         | 8                   | 64             |
|                  | 16                  | 64             |
|                  | 20                  | 69             |
| NaOH (1M)        | 8                   | 53             |

<sup>a</sup> Initial As concentration: 100 µg/L; 100 mL, volume used; amount of Oyster shell: 6.0g; treatment flow rate: 1.7mL/min and volume of desorption agent: 50 mL; No. of analysis for each sample (n)=3

### Application of the optimized treatment system

The utility of the waste oyster shell was evaluated for the treatment of As contaminated groundwater samples and the optimized conditions are presented in Table 2. Water samples were collected from three villages of Kalkini at Madaripur district is 76 kilometers away from capital Dhaka city. The river Padma flows near this areas. Tube well water was collected in polythene containers which were washed before collecting samples with 5% HNO<sub>3</sub>, distilled de-ionized water and finally rinsed with the tube well water at the sampling sites. Total arsenic and other chemical species in these samples were analyzed with Atomic Absorption and UV-Visible Spectrophotometry. The concentrations of total arsenic in the samples were 216.11µg/L, 210.50µg/L and 242.38µg/L respectively. The pH of these groundwater samples was around 7, the arsenic species might be HAsO<sub>4</sub><sup>2-</sup>, H<sub>2</sub>AsO<sub>4</sub><sup>-</sup> for As(V) and H<sub>3</sub>AsO<sub>3</sub> for As(III) [31-33]. The treatment results are presented in Table 3. In Table 3, it is found that the concentrations of arsenic in the treated sample water were lowered to 20.40µg/L, 25.22µg/L and 22.36µg/L respectively. The desorption efficiencies with 100 mL of 2 M KOH were 84%, 86% and 80%. From the present results, the arsenic was successfully removed from real As-contaminated groundwater, and the adsorbed As could be recovered from the surface of oyster shell.

**Table 2.** Optimized conditions for removal of arsenic onto multilayer.

| Name of the parameter | Optimized value |
|-----------------------|-----------------|
| Particle size         | <355 µm         |
| Adsorbent amount      | 6.0 g           |
| Flow rate             | 1.7 ml/min      |
| Initial concentration | 100 µg/L        |
| Initial volume        | 100 mL          |
| pH                    | 6.5             |
| Desorption            | 2M KOH          |

**Table 3.** Removal and desorption of As from the contaminated groundwater of Bangladesh<sup>a</sup>.

| Sample No. | pH   | Initial As concentration (µg/L±SD) | Final As concentration (µg/L±SD) | Removal (%) | Desorption (%) |
|------------|------|------------------------------------|----------------------------------|-------------|----------------|
| 1          | 6.58 | 216 ± 2                            | 20.4 ± 1.2                       | 90.56       | 84             |
| 2          | 6.89 | 211 ± 4                            | 25.2 ± 1.4                       | 88.02       | 86             |
| 3          | 6.66 | 242 ± 4                            | 22.4 ± 1.5                       | 90.77       | 80             |

No. of analysis for each sample (n)=3

<sup>a</sup>Amount of oyster shell: 6.0 g; particle size : <355µm ; flow rate: 1.7 mL/min; desorption: 2 M KOH, 100 mL and standing time: 16 hour

### Distribution of ions in the water

In order to understand the equilibrium concentrations of ionic species in tube well water and treated water, concentrations of some species were also determined: these are presented in the Table 4.

| Well no.         | [Na]   | [Mg]   | [K]    | [Ca]   | [Fe]   | [As]   | [PO <sub>4</sub> <sup>3-</sup> ] | [Cl]   | [SO <sub>4</sub> <sup>2-</sup> ] |
|------------------|--------|--------|--------|--------|--------|--------|----------------------------------|--------|----------------------------------|
|                  | (mg/L) | (mg/L) | (mg/L) | (mg/L) | (mg/L) | (µg/L) | (mg/L)                           | (mg/L) | (mg/L)                           |
| Before treatment |        |        |        |        |        |        |                                  |        |                                  |
| 1                | 18.51  | 12.84  | 5.70   | 28.29  | 1.05   | 216.11 | 2.07                             | 0.82   | 4.01                             |
| 2                | 17.20  | 10.24  | 6.12   | 26.22  | 1.20   | 210.50 | 2.50                             | 0.61   | 4.12                             |
| 3                | 15.52  | 8.52   | 5.52   | 29.20  | 1.02   | 242.38 | 1.56                             | 0.64   | 4.05                             |
| After treatment  |        |        |        |        |        |        |                                  |        |                                  |
| 1                | 10.25  | 13.04  | 4.80   | 29.87  | 1.02   | 20.40  | 1.98                             | 0.75   | 2.01                             |
| 2                | 11.02  | 14.20  | 4.92   | 30.21  | 1.05   | 25.22  | 1.82                             | 0.81   | 1.98                             |
| 3                | 10.22  | 14.25  | 4.88   | 29.56  | 1.02   | 22.36  | 1.80                             | 0.76   | 2.22                             |

pH: (6.58-6.89); temperature: 22°C; n=3

**Table 4.** Average concentrations of major cations and anions of well water.

The concentrations of most of the metals decreased after treatment as presented in Table 4. Arsenic concentrations in all the treated water were all

below 50 µg/L, the Bangladesh standard. These results confirm that the column treatment system is appropriate and suitable for the removal of inorganic As despite its simplicity, easy operation. Residual As concentrations in the treated water show considerable temporal variability as well as consistent differences in removal efficiency.

In addition, the column treatment system not only reduced the As concentration but also reduced K, Fe and SO<sub>4</sub><sup>2-</sup> in treated water. However, PO<sub>4</sub><sup>3-</sup> concentration was not always decreased and Cl<sup>-</sup> concentration was increased in the treated water. This might be due to the oyster shell itself contained higher amount of phosphate. Moreover, NaCl has been added by the commercial oyster shell seller in Bangladesh due to increase the nutrient value in it as poultry feed. While the concentration of Na<sup>+</sup> was decreased by more than 40%, the concentrations of Mg<sup>+2</sup> and Ca<sup>+2</sup> were increased significantly. This is due to the adsorbents which contained Ca and Mg in high concentrations. The measurements show that, on average, treated water satisfy both WHO and U.S. and EPA standards for all inorganic constituents of health concern.

### Conclusion

The proposed column treatment systems are appropriate and suitable homemade approaches to arsenic removal in local areas, because of their simplicity and easy operation and handling. The materials (oyster shell) used as adsorbents for the removal of arsenic from water without any chemical treatment. Therefore, this method would be a very suitable arsenic removal method for a developing country. The present method is effective for a wide range of concentrations, which were quite similar to those observed in contaminated Bangladeshi groundwater. No secondary- pollution problem will occur, because desorption of the arsenic is possible. Direct removal of both arsenite and arsenate can be achieved without first oxidizing arsenite to arsenate, whereas the traditional methods require the oxidation process, thus oyster shell would become a promising simple adsorbent for the removal of arsenic.

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