# LEACHABILITY OF ARSENIC FROM WASTES OF ARSENIC REMOVAL UNITS USING MODIFIED TOXICITY CHARACTERISTIC LEACHING PROCEDURE

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**Abstract:** The present study evaluated the leaching of arsenic from sludge/waste of seven SONO filters that were operated in Rajarampur of Chapai Nawabganj district. For this, Toxicity Characteristic Leaching Procedure (TCLP) test was performed. To understand actual leaching of arsenic, a Simulated Natural Column (SNC) that is comparable to natural mature landfill was devised. Total arsenic concentration ( $As_T$ ) was measured by HG-AAS. The studied arsenic waste/sludge, having 7.0-9.2% solid content, were alkaline in nature (pH values of 7.9-8.7) and had arsenic and iron concentrations of 4.54-5.50 and 480-1039 mg kg<sup>-1</sup> respectively. The TCLP test reveals that 6.4-19.4% (average 14%) of arsenic was leached from the waste (average leachate  $As_T$  before and after TCLP were 5.04 and 0.71 mg kg<sup>-1</sup> respectively). After 102 days of continuous operation in SNC,  $As_T$  in the leachate was found to be 0.223 mg L<sup>-1</sup>, although initial  $As_T$  was 0.350 mg L<sup>-1</sup>. It was observed that  $As_T$  in SNC leachate increased up to 54 days (corresponding to 1.741 mg L<sup>-1</sup>) and then decreased in reciprocal quadratic pattern. Comparison shows that TCLP underpredicts 14.2% of arsenic leaching than that of SNC. Since leachate  $As_T$  in both methods did not exceed the USEPA regulated level of 5 mg L<sup>-1</sup>, the studied waste/sludge was not hazardous.

**Key words:** Arsenic, leaching, TCLP, arsenic removal unit, arsenic waste/sludge, modified column.

misk: eZŷb AaʿqYW PucB besellä kntii iskuigcti KhfZ mZW ntbvwlēttii AveRBi Atmâk yirs-Gi gj "uṭbi jt¶" m=um`z ntqtQ Gi Rb' Toxicity Characteristic Leaching Procedure (TCLP) cix $\|v\|$  Kiv ntqtQ AtmâtKi cüz yirs e\$tZ Simulated Natural Column (SNC), hvcvKyZK cuic° j "Wwltji ngK $\P$ , "cb KivntqtQ |v| AtmâtK NbgvV( $A_{ST}$ ) HG-AAS bivwYYZ ntqtQ AavZ AtmâtK AveRBy htZ 7.0-9.2% KWb `ë w`gb, |v| Qib 7.9-8.7) Ges w`gb AtmâtK I tj\$n NbgvV h\_\text{utg 4.54-5.50 I 480-1039 mg kg-1} TCLP cix|v| Lu th, AveRBi AtmâtKi 6.4-19.4% (Nto 14%) yirsthW (TCLP cixvVi Atm I cti wentz zitj  $A_{ST}$  h\_\text{utg 5.04 I 0.71 mg kg-1} SNC-G 102 with Averig Actikthi ci cix zitj  $A_{ST}$  Qj 0.223 mg L-1, hw`I c\vec{u}yK zitj zv\vec{u}\$ 0.350 mg L-1 \ T Lv \text{1NtQ}, SNC wentz zitj  $A_{ST}$  54 wb ch \(\text{eye} cu \text{(nte/Pgyb 1.741 mg L-1) Ges zvici Reciprocal Quadratic c'\text{Utb}nmcu| TCLP, SNC-Gi zjbu 14.2% AtmâtK yirs Kg f` Lu| thtnzzDfq cxuzi wentz zitj  $A_{ST}$  USEPA wqwz gulv (5 mg L-1) Auz\(\text{u}g Kti by tntnzzAauz AveRb\(\text{S})KcV\(\text{0}\)

## Introduction

Arsenic contamination in groundwater has become a health hazard for a large population of Bangladesh, West Bengal of India and other countries of the world such as Argentina, Chile, Taiwan, Japan and China (BGS 2001; WHO 2001). In Bangladesh, an estimated 24 million people are directly exposed to arsenic contamination and another 75 million are at risk (Engconsult Limited 2002). Nearly 7,600 patients have been identified and a few deaths related to arsenic diseases have also been reported (Engconsult Limited 2002; SOES-DCH 2000; Fazal *et al.* 2001). Evidently, Bangladesh is facing probably the largest mass poisoning in history.

To combat the arsenic problem, the Government of Bangladesh with the support of international agencies as well as local and international NGOs has launched a number of programs. This was done mainly by introducing different types of arsenic removal units (ARUs), e.g., Shapla, SONO (3-Pitcher) filter, ALCAN filter, Bucket Treatment Unit (BTU), SIDKO, etc., that work on the principle of chemical adsorption. The adsorbing materials involved include activated alumina, charcol, iron coated sand, iron coated brick chips and titanium (IV) oxide (Ali and Ahmed 2002). After repeating treatment of contaminated water, the adsorbing materials become saturated by continuously adsorbing arsenic and other materials. The used filter materials (arsenic sludge/waste) are then thrown out in a nearby ditch, latrine or open field without considering geological, hydrological, geochemical environmental aspects that supports traditional arsenic waste disposal method in Bangladesh. This might adversely affect aquatic organisms such as bottom dwelling fishes, agricultural products, ecosystem and the environment of Bangladesh. This demands the sludge/waste to be tested for leaching of arsenic under natural conditions.

The TCLP (Toxicity Characteristic Leaching Procedure) is designed to determine the mobility of both organic and inorganic analytes present in solid, liquid and multiphasic wastes. If one or more compounds of a waste exceed the US Environmental Protection Agency (USEPA) defined regulatory levels, the waste is considered to be hazardous (USEPA 1992). The TCLP test involves mixing the waste with acetic acid solution for 18 hours. The resulting TCLP extract is filtered, acid digested, and analyzed. If the TCLP extract has lower than 5 mg As L<sup>-1</sup>, the waste is considered to be non-hazardous (EHSO 2007).

It is reported (USEPA 1996) that TCLP test underestimates leachate for some high alkaline wastes. This is due to low chelation activity of the TCLP acetate buffer or not considering redox reactions that occur in landfills. The State of California developed one alternative to the TCLP, named California WET (Waste Extraction Test) (Hooper et al 1998). To seek a suitable alternative, Ghosh et al in 2006 conducted detailed studies on leaching of arsenic from granular ferric hydroxide residuals under mature landfill conditions. In that work they simulated the biological physicochemical conditions of a mature, mixed solid waste landfill. They operated a column and found that during the early stages of operation, most of the arsenic and iron were leached (80% and 65%, respectively). Itle (2006) found that the percent solids and age of the residual could affect the test results. Eriksen (2002) investigated 15 NGO-led arsenic mitigation projects in 11 districts of Bangladesh and identified no hazardous leachate from the sludge produced from these units. Badruzzaman (2006) collected arsenic laden waste samples produced from Bucket Treatment Unit (BTU), buried in mud or mixed with organic matter for studying the anaerobic leaching of arsenic in a closed system. He suggested that a significant amount of arsenic was lost through bio-methylation.

After implementation of SONO filter no significant study has been carried out in Bangladesh to assess the leaching characteristics of the wastes produced. Since ARUs residuals might contain concentrated amounts of arsenic, the characterization and toxicity testing of the residuals are important. To understand the appropriate management of arsenic sludge/waste and to address the safety of human health led us to conduct this investigation.

Present work was carried out with two methodologies, namely (i) TCLP test and (ii) Leachability test considering mature landfill condition. These allowed us

to evaluate actually whether a spent filter (arsenic sludge/waste) when dumped in traditional manner would create serious environmental problems in Bangladesh or not, both in short and in long term considerations.

### **Materials and Methods**

Site selection: The study area is situated at the northwestern part of Bangladesh, namely, Rajarampur locality of Nawabganj Sadar thana of Chapai Nawabganj District. The study area is located roughly between 24°34′ N to 24°35′ N and 88°15′ E to 88°18′ E that covers an area of about 4.5 sq. kilometer (Fig. 1). The study area is accessible by concrete roads. Seven samples of arsenic sludge/waste were collected from the SONO filters (Fig. 2) that were being used by the affected people of the Rajarampur locality of Chapai Nawabganj district.

Materials: The chemicals used in this investigation were of high purity analytical grade. Distilled deionized water (DDW), obtained through the deionization plant (TYP-2500, Deng Yuan, China), was used throughout. Perkin Elmer pure atomic spectroscopy standard solution (Perkin Elmer, USA) of arsenic (CAS # 7440-38-2) was used for calibration of arsenic. A number of standard solutions, reducing solutions, buffer solutions, ternary acid mixture and other solutions were prepared according to respective standard procedures (APHA 1995; Hesse 1994; Shimadzu). The other reagents were from Merck (Germany), Fluka (Switzerland) and Sigma Aldrich (USA). Two extraction fluids, used in the TCLP test, were prepared as follows:

Extraction fluid-1: It was prepared by dissolving 5.7 ml of glacial acetic acid (Sigma Aldrich, USA) in 1L measuring flask containing 500 mL of DDW and 64.3 ml of 1M sodium hydroxide (Merck, Germany) solution was added and made up to the mark with DDW. The pH of the final fluid became 4.95.

Extraction fluid-2: It was prepared by dissolving 5.7 ml of glacial acetic acid (Sigma Aldrich, USA) in 1L measuring flask containing 500 mL of DDW and was made up to the mark with DDW to a volume of 1 liter. The pH of the final fluid was 2.9.

For the detection of total and fecal coliform LES M-Endo Agar (Hi-Media, India) and Fecal Coliform M-FC Agar (Hi-Media, India) were used respectively. The cultural media were prepared according to the standard procedures (APHA 1995).

TCLP tests: First preliminary TCLP evaluations were performed with a minimum 100 g of semi-solid waste for: (1) Determination of percent solids, (2) Determination of whether the solid portion of the waste requires particle size reduction or not and (3) Determination of which of the extraction fluids are to be used for the TCLP test.

For determining percent solid in the arsenic sludge/waste, a 100 g of homogeneously mixed semisolid arsenic sludge/waste was transferred to the previously weighed cellulose filter paper (0.8 µm pore size) placed on the ceramic filter holder. After filtration with vacuum pump, the weight of the solid phase of the samples was determined by subtracting the weight of the liquid phase from the weight of the total waste sample. The percent solid was calculated as follows: Percent Solid = (Weight of solid / Total weight of waste) × 100. Since the particle size of the samples was smaller enough to pass through a 9.5 mm standard sieve, the particle size reduction of the wastes was not performed. To determine appropriate extraction fluid, 5.0 g of the solid phase (fresh weight) of the waste was transferred to a 500 mL beaker and 96.5 ml of DDW was added to it. Then it was covered with a watch glass, stirred vigorously for 5 minutes using a magnetic stirrer followed by measuring pH of the samples. Since pH of all the samples were greater than 5.0, extraction fluid-2 were used for the TCLP test. The amount of extraction fluid-2 needed to add to the extraction vessel was determined as follows: Weight of extraction fluid = (20 × weight of waste filtered) / 100.

The filtrate obtained from semi-solid sludge is defined as 1<sup>st</sup> liquid phase. The solid materials obtained were then transferred to the extractor bottle of rotary agitation device and the appropriate amount extraction fluid-2 was added to the extractor vessel slowly. The extractor bottles were tightly closed (Teflon tape was used to ensure a tight seal) and rotated at 32 rpm for 18±1 hours at room temperature of 30°C. To relieve the excess pressure due to formation of gases such as carbon dioxide and methylated arsenic, the extractor bottle were opened after definite interval (e.g., after 15, 30 and 60 minutes). The materials in the extractor vessel were separated in to its component liquid and solid phases by filtering through a cellulose filter. The filtrate obtained is defined as the TCLP extract (2<sup>nd</sup> liquid phase). For

further analyses, e.g., for determining total arsenic concentration (As<sub>T</sub>), the extracted liquid samples were acidified with HNO<sub>3</sub> to keep pH <2 and kept refrigerated at 4°C. The individual phases were then analyzed separately for which the volume of the individual phases were determined. Final analyte concentration was determined using the following formula: Final analyte concentration = [ $V_1C_1 + V_2C_2$ ] / ( $V_1+V_2$ ) where,  $V_1$  and  $V_2$  are the volumes of 1st and 2nd phase liquids respectively,  $C_1$  and  $C_2$  are the concentrations (mg L<sup>-1</sup>) of 1st and 2nd phase liquids respectively.

Leaching tests under Simulated Natural Column (SNC): The natural disposal conditions considered in the study include on land disposal in typical non-hazardous landfill dump or backyard and dumping in household ditch. Microbially active, mildly alkaline, anaerobic conditions characterize mature landfill (Christensen et al 2001). In the experimental section a PVC column, 30 inch in length and 6.3 inch in diameter, was operated in down flow mode (Fig. 3). A syringe delivered 0.35 mL/min of influent, maintaining the water level at a total saturated bed volume of about 13 L. The column was operated at room temperature of 30°C. 5 cm thick pea gravel layers (0.4-1.0 cm diameter) were provided above and below of the active bed ensuring even flow distribution. The active bed was composed of a mixture of 2.5 L arsenic sludge/waste, 3.0 L of anaerobic digester sludge, 5.9 kg of pond mud, 2.5 kg of Domar sand, 2.0 kg of brick chips, and 750 g of paper. Each component was lightly hand mixed before loading. Anaerobic digester sludge was collected from the Biogas plant of Bangladesh Agricultural Development Corporation (BADC), Rajshahi for natural organic matter. Pond mud was collected from the Jungle Genome Tank of the Institute of Biological Sciences, Rajshahi University, which was also organic matter enriched. Paper stripes of 90 g offset paper of about 2.5-3.0 mm wide were used. The papers were soaked in DDW and squeezed to pulp prior to mixing with the other components. Domar sand and brick chips were used for maintaining the porosity and even leaching. The effluent samples were collected from SNC after every three days interval. The samples were acidified to a pH<2 to avoid precipitation and kept refrigerated.

Characterization of sludge, materials of SNC and feed water: The arsenic waste/sludge of SONO filters were characterized by measuring solid content, pH, redox potential, concentrations of arsenic and iron. The materials of SNC and feed water were characterized by measuring pH, redox potential, electrical conductivity,

dissolved oxygen, total dissolved solids, concentrations of arsenic, iron, calcium and magnesium, total coliform and fecal coliform. All the parameters were measured using standard procedures and properly calibrated instruments.

Extraction and analysis for metal concentrations: Prior to analysis of water samples for total arsenic (As<sub>T</sub>) and total iron (Fe<sub>T</sub>) the aqueous samples were subjected to mild digestion with HNO<sub>3</sub> (APHA 1995). But the water samples were not pretreated for estimation of calcium and magnesium. For estimation of As<sub>T</sub>, Fe<sub>T</sub>, Ca and Mg in soil samples, these were digested with H<sub>2</sub>SO<sub>4</sub>-HClO<sub>4</sub> acid mixtures (Sakamoto et al 2001; Hesse 1994; Shimadzu). The digestates after dilution were analyzed for As<sub>T</sub> by Hydride Generation-Atomic Absorption Spectroscopy (HG-AAS) and for Fe<sub>T</sub>, Ca and Mg by Flame-AAS using a Shimadzu-AA 6800 (Shimadzu Corporation, Kyoto, Japan) atomic absorption spectrophotometer. Prior to analysis by hydride generation, 1.5 mL of 37% (v/v) HCl, 1.0 mL of 3% (w/v) KI (containing 3.0 g KI and 5.0 g L(+)-ascorbic acid in 100 mL water) and 5.0 mL of DDW were added to 10.0 mL of the digestates and allowed to stand for 30 minutes to reduce As(V) to As(III).

Microbiological examination: Membrane filter (MF) method was used to count total and fecal coliform bacteria. A volume of 100 ml water was filtered through gridded nontoxic Nitrocellulose membrane filter (Millipore, USA), 47 mm in diameter having pore size of 0.45 μm, under manual vacuum condition. It was placed in a glass Petri dish, with support of absorbing pad, containing 4 ml of the specific cultural media and incubated in a B-28 incubator (Binder, Germany) for 24 h at 35°C for total coliform and 44.5°C for fecal coliform. Finally the produced colonies were counted with the aid of a microscope.

Instrumentation: The atomic absorption spectrophotometer used in the investigation was Shimadzu-AA 6800 (Shimadzu Corporation, Kyoto, Japan) that can run with AA WizAArd software in both graphite furnace and flame mode. The system was equipped with an autosampler ASC-6100 (Shimadzu, Japan) and a hydride vapor generation system HVG-1 (Shimadzu, Japan). The HVG-1 comprises the peristalsistic pump that is used to send the sample, 5M HCl and 0.4% NaBH<sub>4</sub> solution to the reaction coil. The instrumental conditions used for As<sub>T</sub> determination by HG-AAS were the following: wavelength, 193.7 nm; slit width, 1.0 nm; lamp mode, BGC-D<sub>2</sub>; lamp current, 12 mA; flame type, Air-C<sub>2</sub>H<sub>2</sub>; fuel gas flow rate, 2.0 L min<sup>-1</sup>; carrier gas, argon; reducing agent, 0.4% (w/v) NaBH<sub>4</sub>

in 0.5% (w/v) NaOH solution, NaBH<sub>4</sub> flow rate, 6 mL min<sup>-1</sup>; and cell temperature, 2200-2300°C.

The rotary agitation apparatus (Fig. 4) used in the investigation was manufactured locally (STAR Engineering Works, Sayedpur) as per specification of the USEPA (USEPA 1992). It is capable of rotating the extraction bottle at 32 rpm in end-over-end fashion. The basic features of the rotary agitation apparatus include steel frame, 3-phase 2HP motor, magnetic starter, steel shaft, bearing and four extraction bottles. The extraction bottles, 2.3 inch in internal diameter and 8.1 inch in length, were made of exclusively type 316-stainless steel (Japan) and were made vacuum and leak proof.

Statistical analyses: The datasets were treated separately for analyzing basic statistical parameters and making cross tabulations and cross plots. The statistical software used in the data analyses includes SPSS (release 13.0) statistical software package (SPSS Inc., Chicago, Illinois, 2004), STATGRAPHICS Centurion XV (release 12.2.14) software (StatPoint Technologies, Inc., Warrenton, Virginia, 2007). Mathematical models were established based upon simple and multiple regression analysis using SPSS, STATGRAPHICS Centurion XV and CurveExpert (release 1.34) and Microsoft Excel (release 12.0.4518.1014, 2006). The models were cross-checked by analyzing ANOVA, P value, r value (Pearson correlation coefficient) and Durbin–Watson statistics.

Quality control: All glasswares were treated with 10% (v/v) HNO<sub>3</sub> for 24 h and then rinsed three times with DDW followed by drying in an oven. Arsenic analysis was carried out following USEPA approved Quality Assurance/Quality Control (QA/QC) plan with a reagent blank, a duplicate and a spike for every 20 samples. The recoveries of arsenic from the environmental samples were 87.05–91.41%. Moreover, after analyzing every 10 samples, readings of standard solutions were recorded to check the instrument.

# **Results and Discussion**

Characterization of arsenic sludge/waste: The solid contents of all the samples of arsenic sludge/waste were found to be 7.0-9.2% (Table 1) with an average value of 8.3% reflecting that the waste/sludge were semi-solid with liquid portion predominated. The pH of the arsenic sludge/waste were 7.9-8.7 (average 8.3), indicating that they were alkaline in nature. This is attributed to the formation of Fe(OH)<sub>3</sub>.

**Table 1.** Characterization of arsenic waste/sludge of SONO filters.

Sample Solid pН Redox Arsenic Iron ID Content Potential conc. (mg conc. (mg (%)(mV) kg<sup>-1</sup>) kg<sup>-1</sup>) SW\* 01 7.0 3.9 5.50 480 SW 02 4.98 7.8 8.1 5.2 690 SW 03 4.7 8.1 8.4 5.19 588 SW 04 8.2 6.6 4.54 1008 8.4 SW 05 8.9 5.17 693 8.4 8.2 SW 06 9.0 8.7 11.3 5.00 957 4.90 1039 SW 07 9.2 8.3 4.1 Average 8.3 8.3 6.3 5.04 779

Table 2. Results of TCLP for total arsenic content.

Sample	Arsenic concentration (mg kg <sup>-1</sup> )			
ID	Before	After	% Released	
	TCLP	TCLP <sup>+</sup>		
WS 01	5.50	0.96	17.45	
WS 02	4.98	0.32	6.40	
WS 03	5.19	0.65	12.52	
WS 04	4.54	0.37	8.15	
WS 05	5.17	0.81	15.67	
WS 06	5.00	0.92	18.40	
WS 07	4.90	0.95	19.38	
Average	5.04	0.71	14.00	

<sup>&</sup>lt;sup>+</sup> represents mg L<sup>-1</sup>.

Table 3. Characterization of materials of simulated column and feed water.

Parameters	Units	Materials of Simulated Column		Feed Water
		Before Leaching Test	After Leaching Test	
Physical			·	
Temperature	<sup>0</sup> C	31.1	26.9	28.0
pН		7.10	6.54	7.33
Redox Potential (Eh)	mV	3.0	34.5	5.8
Dissolved Oxygen (DO)	mg L <sup>-1</sup>	2.2	1.9	7.4
Electrical Conductivity (EC)	μS cm <sup>-1</sup>	2300	160	766
Total Dissolved Solids (TDS)	mg L <sup>-1</sup>	1472	103	491
Chemical	-		•	
Total Fe concentration	mg L <sup>-1</sup>	1200	135	3.95
Total As concentration	mg L <sup>-1</sup>	7.5	2.0	0.006
Ca concentration	mg L <sup>-1</sup>	70	29	126
Mg concentration	mg L <sup>-1</sup>	36	24	87
Bicarbonate (HCO <sub>3</sub> <sup>-</sup> ) conc.	mg L <sup>-1</sup>	-	-	369
Aicrobiological	- 1		•	
Fecal Coliform	CFU/100 g	$1.9 \times 10^5$	$0.3 \times 10^5$	0
Total Coliform	CFU/100 g	70.0 x 10 <sup>5</sup>	$5.4 \times 10^5$	0

The total arsenic concentrations of the studied waste/sludge ranged 4.54 - 5.50 mg kg<sup>-1</sup> on fresh weight basis (average 5.03 mg kg<sup>-1</sup>). The value is typical in the soil or sediment arsenic content in Bangladesh (BGS/DPHE, 2001). Total iron concentrations of the arsenic waste/sludge were abnormally high, 480-1039 mg kg<sup>-1</sup> (average 779 mg kg<sup>-1</sup>). The probable reasons for the high values include use of iron containing materials in SONO filter, high concentration of iron in feed water

and formation of Fe(OH)<sub>3</sub> flocks during treatment operation to which arsenic is adsorbed.

TCLP analysis: The concentrations of arsenic of the waste/sludge of the studied seven SONO Filters before and after TCLP test along with percent arsenic released are reported in Table 4.4. The data suggested that only 6.4 - 19.4% of arsenic was leached after performing TCLP. The arsenic concentration in TCLP extract was below 1.0 mg kg<sup>-1</sup> in all cases (Fig. 4.3).

<sup>\*</sup> SW stands for arsenic waste of SONO filter.

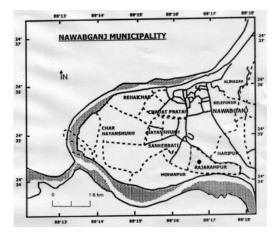




Fig. 2. A SONO filter.

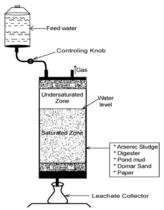


Fig. 3. Schematic diagram of simulated natural column (SNC).

Fig. 1. Location map of the study area.



Fig. 4. Rotary agitation apparatus.

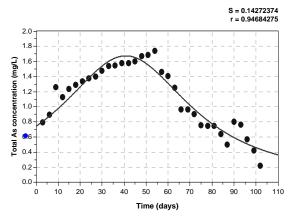
For arsenic (EPA Hazardous Waste Code D004), the regulatory level is 5.00 mg kg<sup>-1</sup> (EHSO, 2007). As the arsenic concentration in the TCLP extract of the solid samples ranged between 0.32 and 0.96 mg kg<sup>-1</sup>, it is apparent that none of the studied arsenic sludge/waste would be toxic or hazardous in nature as per the standard of the USEPA. This means that the arsenic sludge/waste can be dumped into the soil without making any significant environmental pollution.

Characterization of materials of simulated column and feed water: When the waste was alkaline, an authentic procedure for leaching test that would provide accurate results under natural landfill conditions demanded. Since the arsenic sludge/waste of the SONO filters are alkaline in nature (average pH value of 8.3), we introduced a simulated column in which anaerobic digester sludge, pond mud, paper, sand and brick chips were introduced in a ratio that was similar to natural landfill conditions. The physical, chemical and microbiological properties of the simulated column materials as well as feed water are presented in Table 3.

Obviously, the simulated column materials were neither acidic nor alkaline. The low values of redox potential and dissolved oxygen indicated that the materials were in reducing environment. The high values of electrical conductivity and total dissolved solids indicated that many potential ions were present in the column materials. The total concentration of arsenic, calcium and magnesium were characteristics of wet land or dumped land of Bangladesh (BGS 2001). But very high value of total iron concentration was observed. The coliform bacteria of order of 10<sup>5</sup> per 100 g of soil indicates microbial activity in the column materials. These facts reflected that the simulated column materials were very close to mature natural landfills.

The feed water was almost neutral (pH 7.33). The high bicarbonate concentration and relatively high concentrations of calcium, magnesium and iron indicated that the water was hard. Hence, high values of electrical conductivity and total dissolved solids were observed. The feed water also contained dissolved oxygen to considerable extent. The total arsenic concentration in the feed water was very low (0.006 mg L<sup>-1</sup>), which is below the WHO guideline value for drinking water (0.010 mg L<sup>-1</sup>). The water did not contain any fecal bacteria to perform microbial activity.

Leaching from simulated column: The leachates obtained from the mature simulated column were collected after every third day interval up to 102 days. The collected samples were acidified, digested with nitric acid and analyzed for total arsenic and iron concentrations. Regression analysis for  $As_T$  showed that the fitted model was Reciprocal Quadratic,  $y = 1/(a + bx + cx^2)$ , where y is total As concentration of leachate in mg  $L^{-1}$  and x time in days (Pearson correlation coefficient, r = 0.947; Fig. 5 a).



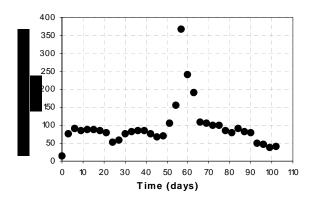
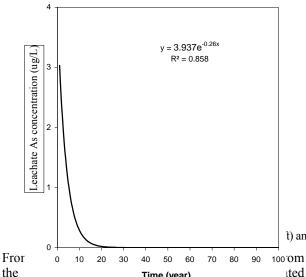
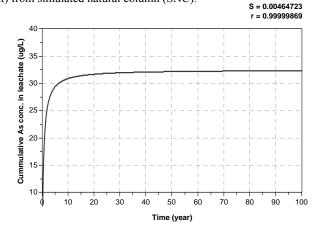


Fig. 5. Leachable arsenic (left) and iron (right) from simulated natural column (SNC).





t) and cumulative as concentrations (right) in the leachates.

the Time (year) column was first gradually raised reached to the maximum (corresponding to the arsenic concentration of 1.741 mg L<sup>-1</sup> at 54<sup>th</sup> day of experiment) and then fell exponentially. The increase in arsenic concentration can be illustrated by the fact that the microbial reduction using dissolved organics from anaerobic digester sludge became very active producing less sorbed As(III) (BGS 2001). After reaching the peak value, the decreasing trend might be explained by the microbial methylation of arsenic to produced volatile compounds of arsenic (Bhumbla and Keefer 1994). This is in agreement with many authors (Shariatpanahi et al 1982; Challenger et al 1933) that reported that several fungi (e.g., Penicillum brevicaulis and Candiada fumicola) and bacteria (e.g., Nocardia sp. and Aeromonas sp.) had been found to methylate inorganic arsenic by an initially reducing arsenate fraction to arsenite followed by methylation and released to the environment. Although noticeable fluctuation was observed, but the ultimate trend was decreasing. Because after 102 days of continuous operation, the arsenic concentration in the leachate became 0.223 mg  $L^{-1}$  although initial concentration was 0.350 mg  $L^{-1}$  and averagely increased for first 40 days and decreased for the rest 62 days.

From Figure 5. b it follows that iron leaching shows a rough fluctuation at different interval of the experiment. Generally, the iron leaching was gradually increased from the beginning to 57 days of the experiment probably due to increase in microbial reduction and enhanced iron leaching (conversion of Fe<sup>3+</sup> to Fe<sup>2+</sup>). The iron leaching was declined with high amount afterwards. The continuous decrease in iron concentration at the end period of the experiment may be a consequence of declining microbial activity.

It was noticed that at any instant the higher arsenic concentration was generally associated with higher iron concentration. This situation might be for the active iron dissolution and recrystallization (Fredrickson et al 1998). As a result, newly precipitated iron phases (magnetite or goethite) had a lower arsenic sorption

capacity than the original arsenic sludge. Moreover, at the end of the experimental period almost major portion of the iron had leached out.

Prediction of leaching with respect to time: Based upon the lechate data, the leachable arsenic concentrations from simulated natural column for different intervals were plotted, the best-fitted model was determined and the extrapolation was made. The determined values were further plotted for leachate arsenic concentration versus time. The fitted model found was exponential,  $y = a.e^{bx}$  (where y was leachate As concentration in  $\mu g L^{-1}$  and x time in year) with r = 0.927 (Fig. 6.a)). This figure gives 100 year projected arsenic concentrations in the leachates. Obviously, the leachate arsenic concentration decreases exponentially with time. For example, after 13 years the estimated arsenic content in the leachate would be less than 0.10  $\mu g L^{-1}$ , although it would be 20.92  $\mu g L^{-1}$  at first year.

The cumulative arsenic concentrations in the leachates were also plotted against time. The regression equations of the fitted model were found in Morgan-Mercer-Florin (MMF) form,  $y = (ab + cx^d)/(b + x^d)$ , with r=0.999 (Fig. 6.b)). It is obvious that most of the arsenic is leached within first 10 years. After 50 years, there will virtually no change in cumulative arsenic concentration in the leachates.

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