Fate of Arsenic in Wastes Generated From Arsenic Removal Units

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INTRODUCTION

Widespread arsenic contamination of groundwater has become a major threat to the water supply sector in Bangladesh. In Bangladesh, an estimated 268 upazillas out of 465 have been affected with significantly high concentrations of arsenic. The southern, central and north-eastern regions of Bangladesh have been most severely affected by arsenic contamination of shallow tubewell water. In Bangladesh tubewell water extracted from shallow aquifers is the primary source of drinking/cooking water for most of its population. An estimated 7.5 to 8.0 million hand-tubewells constitute the backbone of the rural water supply in Bangladesh. The urban water supply is also heavily dependent on groundwater. An estimated 28 million people are exposed to arsenic concentrations in tubewell water above the Bangladesh drinking water standard of 50 ppb (Begum, 2001).

To combat the arsenic crisis, a number of household and community based arsenic removal technologies have been developed and a number of such technologies are currently being used in many arsenic affected areas. All arsenic removal units generate some form of arsenic-rich wastes. In the absence of any clear guideline for safe disposal of wastes generated from arsenic removal units, such wastes are often disposed in the open environment. Broadly, the arsenic-rich waste materials can be classified into: (a) wastes generated from coagulation based systems,

and (b) wastes generated from systems based on adsorptive filtration and others techniques (e.g., ion exchange). The waste belonging to the first category is primarily slurry containing coagulated flocs of alum or iron salt, rich in arsenic. Currently, disposal of such wastes in cow-dung bed is widely practiced. It has been suggested that biochemical processes in cow-dung bed transform inorganic arsenic and release it into air. However, data supporting such processes are scant. The wastes belonging to the second category are primarily spent adsorption/ion-exchange media, rich in arsenic. With increasing use of arsenic removal units, concerns have been raised regarding safe disposal of these wastes and possible contamination of environment from arsenic present in the wastes. However, there is only limited data on the quantities and characteristics of these wastes (e.g., Hamel and Zinia, 2001) and possible mobilization of arsenic from these wastes.

The major objective of this present study is to evaluate the fate of arsenic in the wastes generated from arsenic removal systems. Specific objectives include: (i) Estimation of quantity of arsenic-rich wastes generated from different arsenic removal units, (ii) Understanding leaching (through TCLP tests) and transformations (in the presence of cow-dung) of arsenic in wastes generated from coagulation based arsenic removal systems, and (iii) Understanding leaching of arsenic from wastes generated from filtration based arsenic removal systems (through TCLP and column studies).

MATERIALS AND METHODS

Collection of Treatment Waste Samples

In this study, wastes generated from different types of arsenic removal systems have been collected, with assistance from BAMWSP, DPHE-Danida and some non-government organizations. Arsenic-rich wastes have been collected from two different types of coagulation-based systems. These are (i) STAR bucket treatment (based on iron coagulation), and (ii) UNU-BUET bucket treatment unit (based on ferric chloride coagulation). All samples have been collected from operational arsenic removal units. Two types of samples were collected from the BUET-UNU units, slurry from the upper bucket and sand filter media from the lower bucket. Wastes from the first type of arsenic removal units were collected from Laksmipur district. Wastes from the UNU-BUET unit have been collected from the UNU-BUET field site at Adda village in Barura Thana of Comilla district. Arsenic rich wastes have also been collected

from three different types of filtration-based arsenic removal systems. These are: (i) "Shapla" filter (based on filtration through iron-coated brick chips), (ii) BUET-UNU iron-coated sand filtration units, (iv) SIDKO granular ferric hydroxide units. All samples have been collected from operational arsenic removal systems. Spent media from "Shapla" filters were collected from Noakhali region, spent iron-coated sand media were collected from Adda village in Barura, Comilla, and spent SIDKO filter media were collected from Manikgonj.

Estimation of Treatment Waste Generation

The quantity of wastes generated from STAR and BUET-UNU bucket treatment units and "Shapla" filters were estimated based on information from the users of these units gathered during field visits to Noakhali, Laksmipur and Comilla.

Leaching Characteristics of Wastes

TCLP tests

In this study, leaching characteristics of wastes collected from different arsenic removal units have been evaluated through Toxicity Characteristics Leaching Procedure (TCLP) developed by the USEPA. TCLP tests were performed for fourteen slurry samples collected from STAR bucket treatment units and for two samples collected from BUET-UNU bucket treatment units. TCLP tests were also carried out for 15 samples from "Shapla" filter, two from BUET-UNU iron coated sand units, two from SIDKO units, and two samples of sand media collected from the BUET-UNU bucket treatment units. All TCLP tests for solid samples were performed in duplicates and averages of the results have been reported here. In all cases arsenic concentrations were measured with a graphite furnace-AAS (Shimadzu AA6800).

Column experiments

In order to evaluate long-term leaching characteristics of treatment wastes, column experiments have been carried out with spent media from "Shapla" filter. A total of four columns were set up and leaching of arsenic from the "Shapla" filter media were evaluated under continuous flow with four different extraction fluids (one for each column). The extraction fluids were: (i) distilled water, (ii) arsenic-free natural groundwater, (iii) rainwater, and (iv) pond water.

For column experiments, collected spent "Shapla" filter media were first well mixed and oven-dried. Grain size analysis of the dried filter media

was performed with sieve analysis, and total arsenic content (in mg/kg) of the media was measured following digestion of a portion of the dried sample. Column experiments were carried out in 1.5-cm inner dia graduated glass columns. In each column, 80-grams of filter media, with a total volume of about 67.3 cm^3, was taken. Extraction fluids were passed through the columns in a down-flow mode with a flow rate of about 39 (± 1.5) ml/hr. The extraction fluids coming out from the columns were collected daily, acidified and tested for arsenic concentration using a graphite furnace AAS (Shimadzu AA6800). The column experiments have been continuing for periods ranging from three to four months.

Transformation of Arsenic in Presence of Cowdung

As mentioned earlier, disposal of treatment wastes in cow-dung bed is widely practiced in Bangladesh. It has been suggested that biochemical processes in cow-dung bed transform inorganic arsenic and release it into air, although data supporting this claim are very limited. In order to assess transformation of arsenic in the presence of cow-dung, batch tests were conducted in 15-ml falcon centrifuge tubes. . Stock solutions of As(III) and As(V) were prepared with Hach-NIST arsenic standards. Aqueous arsenic solutions (12 ml) with known concentrations (varying from 80 ppb to 500 ppb) of either As(III) or As(V) were taken in a series of tubes (a total of 8 to 10 tubes for each set of experiment). Fixed quantities (1, 2 and 6 grams) of fresh cow-dung were added to each of the tubes. One set of tubes was capped and a similar other set was left uncapped. After particular intervals, one tube from each set was taken out and centrifuged to separate the solid (cow-dung) from the liquid. The capped tubes were uncapped and left open for sometime. The liquid portion from each tube was then separated by decanting and its arsenic concentration was measured (after acidification). Arsenic content of the solid (cow-dung) portion was also determined after digestion with aqua-regia. Arsenic content of freshly collected cow-dung was also determined after digestion. Thus total arsenic present in the tubes were determined as a function of time to see any change in total arsenic content in the presence of cow-dung

In order to assess transformation of arsenic present in treatment wastes in the presence of cow-dung, similar experiments (as described above) were conducted with slurry wastes collected from both STAR and BUET-UNU bucket treatment units. At first, arsenic contents of well mixed slurry wastes collected from both types of units were determined after digestion with aqua-regia. For batch experiments, fixed volumes of slurry wastes (5-ml for STAR-waste and 30-ml for BUET-UNU-waste) were taken in a series of 50-ml falcon centrifuge tubes (a total of 8 to 10 tubes

for each set of experiment). Fixed quantities (2, 4 and 8 grams) of freshly collected cow-dung were added to each of the tubes. One set of tubes was capped and a similar other set was left uncapped. After particular intervals, one tube from each set was taken and arsenic concentration of its contents was determined after digestion (with aqua-regia). As before, arsenic content of freshly collected cow-dung was also determined after digestion. Thus changes in total arsenic content in the tubes were determined as a function of time. In all cases arsenic concentrations were measured with graphite-furnace AAS (Shimadzu AA6800).

RESULTS AND DISCUSSION

Estimation of Treatment Waste Generation

Amount or quantity of waste generated from arsenic removal processes was evaluated for three types of household arsenic removal systems. These are: (i) BUET-UNU bucket treatment unit, (ii) STAR bucket treatment unit, and (iii) "Shapla" filter. In the BUET-UNU bucket treatment unit, a chemical packet (containing ferric chloride, potassium permanganate and bleaching power) is added to 25 liters of water in the upper bucket of the unit. After stirring the water is kept undisturbed for about one hour, and then the water is allowed to flow to the lower bucket through a tap located at the bottom of the bucket. hformation gathered from the field suggest that after each run, about 24.5 liters of treated water is produced and about 500 ml of slurry containing mainly (arsenic-rich) ferric hydroxide flocs accumulate at the bottom of the upper bucket, which is later disposed of. Thus, waste generation rate for this unit is about 500 ml slurry per 24.5-liters of treated water. The STAR filter runs on a similar principle. However, information gathered from the field suggest that most users dispose of the slurry (accumulated at the bottom of the bucket) after treating two or three buckets of water. It was estimated that on an average about 250 ml of slurry waste is generated per 40-liters of treated water.

In each unit of "Shapla" filter, about 20 kg of filter media (iron-coated brick chips) is used for treatment of water. This media can treat about 3000 to 6000 liters of water (depending on arsenic and other water quality parameters). The media is discarded after exhaustion. Thus, on an average, 20-kg of arsenic-rich spent media is produced for 4500 liters of treated water. Good estimates of some other types of arsenic removal units (e.g., SIDKO granular ferric hydroxide units, BUET-UNU iron-coated sand units) could not be obtained due to lack of reliable field data.

Leaching Characteristics of Treatment Wastes: TCLP Tests

TCLP test results of slurry wastes collected from STAR and BUET-UNU bucket treatment units are presented in Table 1. In the 14 slurry samples collected from operational STAR units, percent solid varied from about 2.5 percent to about 20.4 percent and arsenic concentration varied from about 1.2 mg/l to about 38.5 mg/l. For both the samples from the BUET-UNU units, solids content was about two and a half percent and initial arsenic content was about 0.9 mg/l. The arsenic content of these wastes primarily depends on the arsenic concentration of the groundwater treated as well as other water quality parameters. Table 1 shows that for majority of the samples from the STAR units, leaching of arsenic expressed as a percent of initial arsenic present is very low. For six samples leaching was less than 1 percent, for six samples it was less than 5 percent. High leaching (23.5 and 37.6 percent) were recorded for only two samples. However, the reason for high leaching from the two samples is not clear. Relatively high leaching was observed for the samples from the BUET-UNU units (21 and 44.2 percent). The TCLP test results shown in Table 1 confirm that the slurry waste samples from arsenic removal units are not "hazardous" as defined by the USEPA.

Table 2 shows TCLP results of 19 solid samples – 15 spent "Shapla" filter media, 2 spent SIDKO filter media and 2 (sand samples) from BUET-UNU bucket treatment units. For these solid samples, leaching of arsenic (also expressed as percent of initial arsenic present) was very low. For the spent "Shapla" filter media, it ranged from 0.69 to 3.3 percent. Leaching from the spent SIDKO media and sand from BUET-UNU bucket treatment units was negligible. None of the solid samples belongs to "hazardous" category, as defined by USEPA.

Leaching Characteristics of Treatment Wastes: Column Experiment

Leaching of arsenic from arsenic-rich spent "Shapla" filter media were evaluated through column tests using four different extraction fluids. Figure 1 shows arsenic concentration in column effluents as a function of bed volume of fluid passed through the columns. It shows that for all extractants, arsenic concentration in the column effluents were initially very high, but then dropped sharply. Figure 2 shows leaching of arsenic from the columns as a function of bed volumes for all four extractants. Of all the extractants, distilled water showed highest level of leaching, followed by groundwater, rainwater and finally pond water. The highest leaching by distilled water appears to be due to the lack of dissolved ions in distilled water. The higher leaching by groundwater compared to rainwater is probably due to the presence of higher level of phosphate in

the groundwater, which may promote desorption of arsenic from the filter media. These issues are currently being investigated in more details.

Table 1: Results of TCLP tests performed on slurry waste samples from STAR and BUET-UNU bucket treatment units

Sl. No.	Sample ID	Name of Treatment Unit	% Solids	As Conc. in Raw Sample (mg/l)	As Conc. in TCLP Extract (mg/l)	% Leaching
1	TCLP-24	STAR BTU	8.8	12.9	0.035	0.27
2	TCLP-25	STAR BTU	16.6	1.4	0.011	0.81
3	TCLP-26	STAR BTU	9.2	38.5	1.255	3.26
4	TCLP-27	STAR BTU	5.2	10.9	0.093	0.85
5	TCLP-28	STAR BTU	3.1	1.7	0.398	23.5
6	TCLP-29	STAR BTU	2.5	6.5	0.199	3.06
7	TCLP-30	STAR BTU	20.4	17.1	0.104	0.61
8	TCLP-31	STAR BTU	8.3	10.8	0.070	0.65
9	TCLP-32	STAR BTU	16.6	30.3	1.124	3.72
10	TCLP-33	STAR BTU	16.1	18.5	0.312	1.68
11	TCLP-36	STAR BTU	6.4	1.2	0.450	37.6
12	TCLP-37	STAR BTU	10.8	24.5	0.143	0.58
13	TCLP-38	STAR BTU	15.0	3.3	0.151	4.59
14	TCLP-39	STAR BTU	18.2	26.2	0.357	1.37
15	TCLP-34	BUET-UNU	2.6	0.90	0.190	21.0
16	TCLP-35	BUET-UNU	2.4	0.93	0.411	44.2

After about 1550 bed volumes, distilled water could leach out about 33 percent of arsenic from the spent filter media in the column; after about 1600 bed volumes, groundwater could leach out about 26 percent, which was closely followed by rainwater and pond water. However, from the nature of the curves in Fig. 2, it is clear that there is little scope of significant further leaching of arsenic from the filter media. The column tests showed significantly higher leaching of arsenic from spent filter media compared to TCLP tests where arsenic leaching varied from only 0.69 to 3.3 percent. Thus it appears that TCLP tests are not appropriate for assessing long-term leaching of arsenic from treatment wastes.

Table 2: Results of TCLP tests performed on solid waste samples from different arsenic removal units

Sample ID	Name of Treatment Unit	Type of Sample	As Conc. in Raw Sample (mg/kg)	As leached with TCLP Extract (mg/kg)	% Leaching
TCLP-2	Shapla	Spent media	38.8	0.46	1.20
TCLP-6	Shapla	Spent media	18.1	0.33	1.81
TCLP-7	Shapla	Spent media	8.0	0.20	2.45
TCLP-8	Shapla	Spent media	37.9	0.26	0.69
TCLP-11	Shapla	Spent media	14.7	0.21	1.46
TCLP-12	Shapla	Spent media	25.1	0.65	2.60
TCLP-13	Shapla	Spent media	23.2	0.27	1.16
TCLP-14	Shapla	Spent media	30.2	0.26	0.87
TCLP-15	Shapla	Spent media	14.2	0.17	1.21
TCLP-16	Shapla	Spent media	9.7	0.32	3.31
TCLP-17	Shapla	Spent media	22.5	0.22	0.96
TCLP-18	Shapla	Spent media	24.5	0.42	1.70
TCLP-19	Shapla	Spent media	19.7	0.20	0.99
TCLP-20	Shapla	Spent media	12.7	0.20	1.61
TCLP-21	Shapla	Spent media	24.8	0.62	2.50
TCLP-9	SIDKO ARU	Spent media	798	0.70	0.09
TCLP-10	SIDKO ARU	Spent media	708	0.99	0.14
TCLP-22	BUET-UNU	Sand	37.0	0.28	0.77
TCLP-23	BUET-UNU	Sand	19.2	0.09	0.47

Transformation of Arsenic in Presence of Cow-dung

Figure 3 shows results of batch experiments conducted to assess transformation of arsenic from aqueous solutions in the presence of cow-dung. These figures show significant elimination of As(III) from aqueous solution in the presence of cow-dung. In most cases elimination of arsenic under cap-open and cap-closed conditions were similar. Majority of this elimination appears to take place during the first few days. These and

other results obtained in this study suggest that the elimination of arsenic is not proportional to the amount of cow-dung added to the aqueous solutions. Similar results were also obtained from experiments with aqueous solutions of As(V).

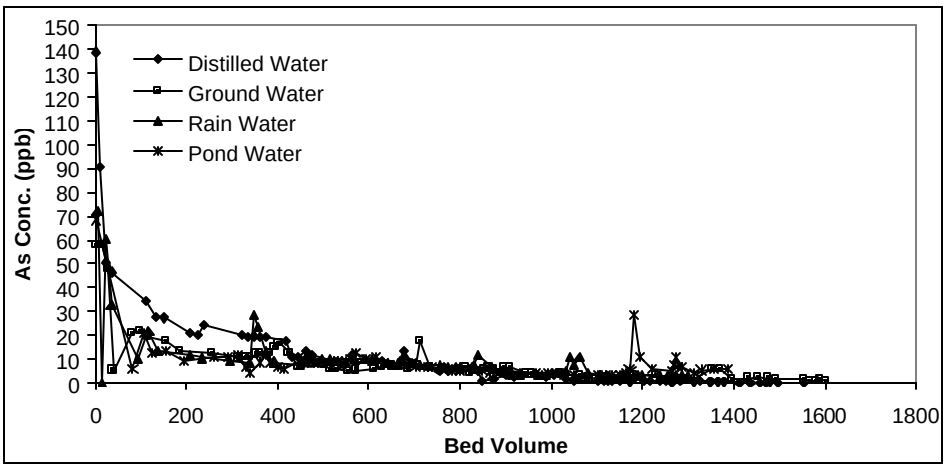

Figure 1: Arsenic in column effluents as a function of bed volume of fluid passed through the columns

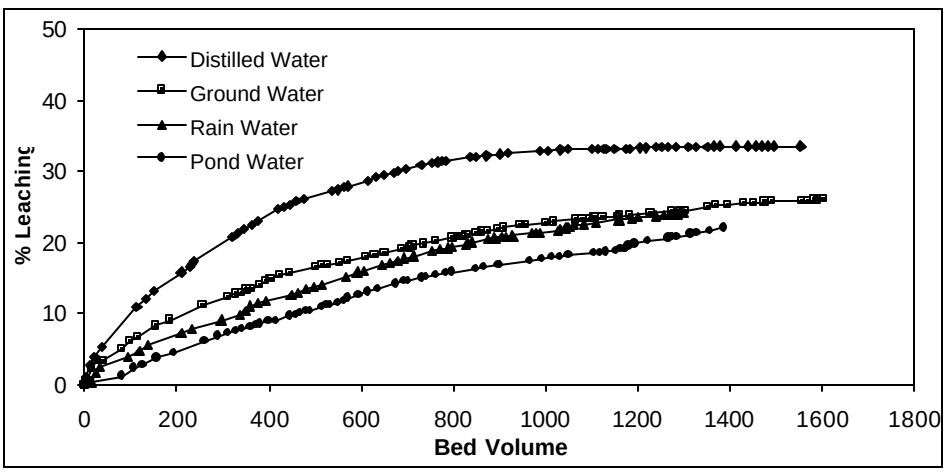

Figure 2: Leaching of arsenic from waste (in terms of % of initial quantity leached) as a function of bed volume of fluid passed through the columns

Figure 4 and Fig. 5 show elimination of arsenic in the presence of cow-dung from treatment wastes from STAR and BUET-UNU units, respectively. Similar to previous results, significant elimination of arsenic from the wastes were observed during the first few days and then arsenic contents appear to reach a plateau. Elimination of arsenic could not be directly correlated with the amount of cow-dung added to the wastes. In most cases, the differences between results under open-cap and closed-cap conditions were similar.

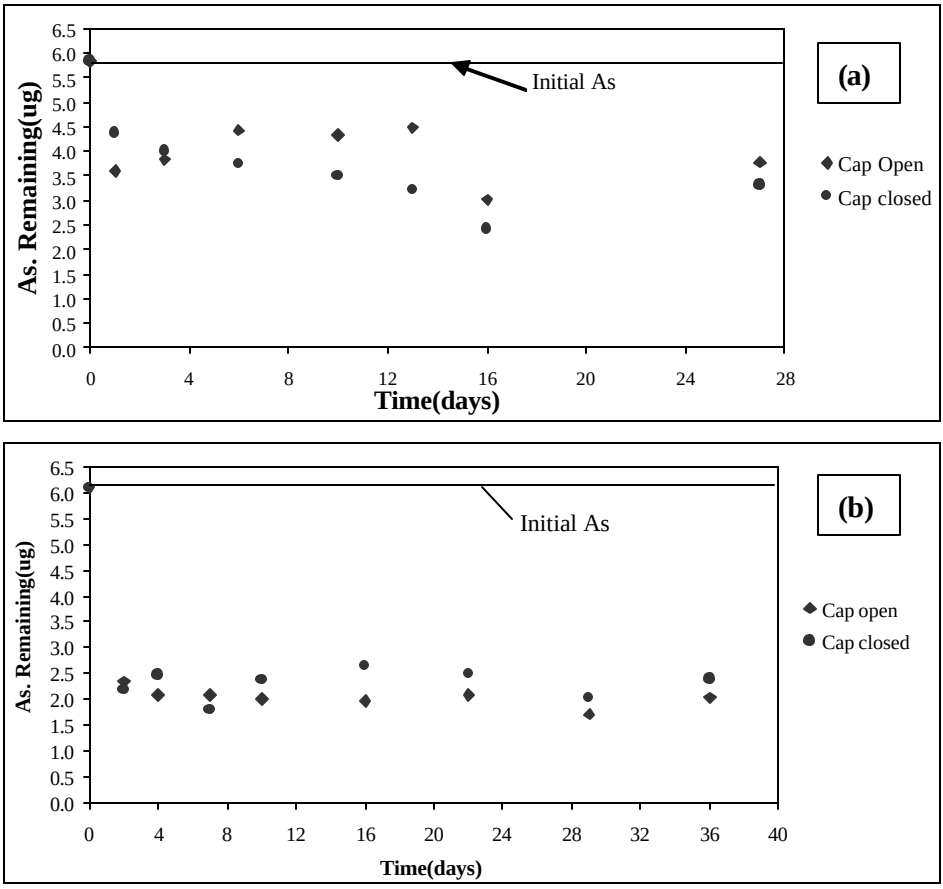

Figure 3: Elimination of As(III) from solution in batch tests in presence of cow-dung: (a) 1-gram cow-dung, (b) 2-gram cow-dung

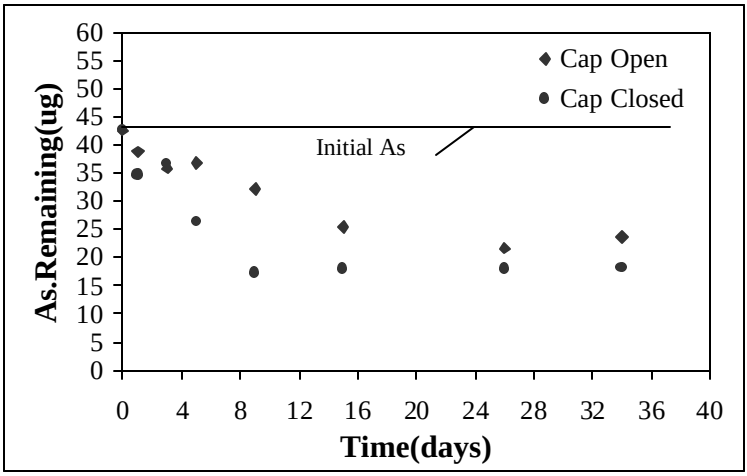

Figure 4: Elimination of arsenic present in treatment wastes from STAR units in the presence of 2-gram cowdung

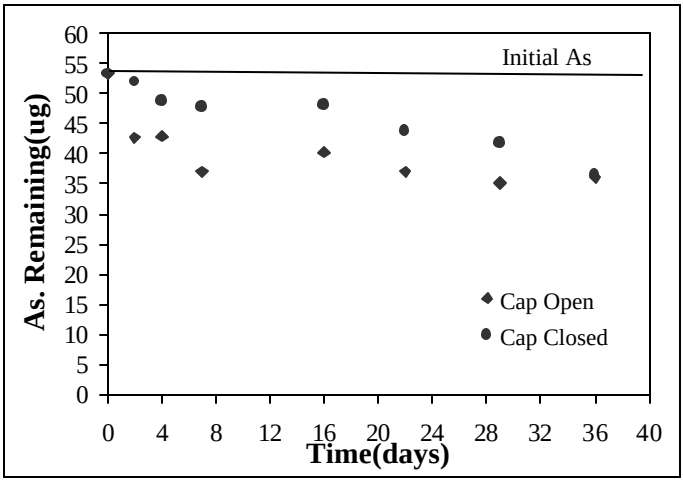

Figure 5: Elimination of arsenic present in treatment wastes from BUET-UNU BTUs in the presence of 2-gram cowdung

Results from this study suggest that bio-chemical (e.g., bio-methylation) process in the presence of fresh cow-dung may lead to significant elimination of arsenic from arsenic-rich treatment wastes.

However, the process appears to slow down significantly with time, under the experimental conditions followed in this study. It should be mentioned that Rahman (2002) investigated elimination of arsenic from treatment wastes in the presence of soil and cow-dung over a longer time periods and observed significant elimination of arsenic during the first one to two months, after which removal rates dropped significantly. More studies are needed to better understand the bio-geochemical processes responsible for transformation of arsenic and factors affecting such transformations.

CONCLUSIONS

Large-scale use of arsenic removal system may generate significant quantities of arsenic-rich treatment wastes and indiscriminate disposal of these wastes may lead to environmental pollution. TCLP tests performed on a wide range of treatment waste samples in this study suggest that, in general, leaching of arsenic from the wastes are not significant and that none of the waste samples are "hazardous" as defined by the USEPA. Among the slurry waste samples, leaching was less than 1 percent (of initial arsenic present) for six samples, less than five percent for six samples, and between 20 and 40 percent for two samples. For the solid samples, leaching of arsenic (also expressed as percent of initial arsenic present) was very low. For the spent "Shapla" filter media, it ranged from 0.69 to 3.3 percent, and for the SIDKO media and sand from BUET-UNU bucket treatment units leaching was almost negligible. However, continuous-flow column experiments with spent "Shapla" filter media suggest that significant amount of arsenic could be leached from such wastes by distilled water, rainwater, pond-water and groundwater. For example, distilled water could leach about 33 percent of arsenic from spent "Shapla" filter media after passage of about 1550 bed volumes; the corresponding leaching by natural groundwater was about 26 percent. Hence TCLP test does not appear to be appropriate for assessing long-term leaching of arsenic from treatment wastes. Results from this study suggest that bio-chemical processes in the presence of cow-dung may lead to transformation of arsenic present in arsenic-rich treatment wastes leading to its elimination from such wastes. However, more studies are needed to better understand these processes and factors affecting such transformation of arsenic.

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