

## Research Article

### Arsenic Sorption Characteristics in Decommissioned Tailings Dam Environment at the Obuasi Mine, Ghana

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**Abstract:** Arsenic (As) sorption characteristics in decommissioned tailings dam environment at the Obuasi mine, Ghana was studied. The aim was to outline effective remediation strategy for As, hence the objectives were to establish: (1) Arsenic degradation capacity of the decommissioned tailings dam environment and empirical model(s) to describe the degradation pattern; (2) relevant equilibrium concentration range and time frame for As degradation by natural attenuation. Eighteen water sampling events from monitoring boreholes were spread over 24 months, while leachate from dynamic leaching experiment of soil/sediment were sampled during 14 sampling events, spread over 30 weeks. The samples were filtered through 0.45 µm cellulose membrane and filtrates analyzed for As concentrations. Results followed reducing mass pattern for both sets of observations. The Freundlich and Langmuir isotherms were applied to both data, with the Freundlich isotherm indicating a strong sorption capacity, with regression gradients of 0.528 and 0.615 and high predictive model ( $R^2$ ) values of 0.842 and 0.912 for both experimental and field data respectively. A t-test statistic established that, equilibrium existed between sorption processes within the media between compliance value ( $C$ ), ranges of 0.50-0.01 mg/L and time period ( $t$ ) of 14.5-45.5 months. The As degradation pattern within both investigated media is governed by the model equation:  $[t_n = -8 \ln(c_n) + 9]$  or  $[t_n = 8 \ln(\frac{1}{c_n}) + 9]$ ; where  $n$  is a variable. The model may be used to evaluate soil sample leaching results from contaminated sites ear-marked for remediation through setting targets and objectives for environmental management plans.

**Keywords:** Arsenic, degradation, isotherms, obuasi mine, sorption, tailings dam

## INTRODUCTION

Labile Arsenic (As) in mining environments is normally stored in temporary sinks such as soils and tailings dams (Wang and Mulligan, 2006). According to Blowes (1997), As from contaminated sites demonstrate high affinity for iron and secondary minerals by the process of adsorption; the As may also be desorbed from adsorption sites into water due to varying geochemical and hydrological processes. Copious desorption of As may result in elevated concentrations and pose increased toxic risk and health issues in the environment (Straskraba and Moran, 2006). Concerns about these impacts may be addressed through the understanding of geochemical processes such as sorption, for the application of remedial actions aimed at attaining site-specific remedial objectives within specific time frames. At most sulphide mines a common remediation procedure to possibly induce metal adsorption through acid neutralization is by the

use of alkaline amendment (Robinson-Lora and Brennan, 2009).

At the Obuasi mine in Ghana, As which is principally derived from arsenopyrite present in the gold sulphide ore has been established as a dominant Contaminant of Concern (COC) (Foli and Nude, 2012). At the mine, sulphide ores are characterized using Acid Base Accounting (ABA) test, to establish net neutralization potential for the prediction of pre-mining water quality (Foli *et al.*, 2011). Furthermore, tailings waste is also characterized for stability prior to disposal into repository, using Toxicity Characterization Leaching Procedure (TCLP) test (Foli *et al.*, 2012). That notwithstanding, Blowes (1997) indicated that in tailings impoundment, series of complex geochemical processes may trigger physico-chemical imbalances which require regular monitoring for As and pH among a host of other parameters for the purpose of actively remediating possible impacts. Dependency on pH for the above purpose is however inadequate since As is highly mobilized in water at near neutral conditions in

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the environment (Foli *et al.*, 2012; Norris, 2005; Kaye, 2005).

Although several active remediation methods abound (Safiuddin and Karim, 2001), implementing them can be relatively expensive (Singh and Singh, 1992; Saharan *et al.*, 1995). Hence a relevant passive remediation method such as sorption will be vital for complementing any active method to manage As impacts. According to Wang and Mulligan (2006), documented mechanisms of attenuation are either rate- or capacity-limited so that contaminants can fully attenuate in terrains that have been earmarked for site clean-ups. Results of adsorption tests are analyzed using linear regression tools and adsorption isotherm equations that relate the amount of solute adsorbed to the equilibrium concentration of the solute (EPA, 2007). However, Bethke and Brady (2000) pointed out that although single parameter distribution coefficient ( $K_d$ ) approach may be used, there may be potential problems, mostly when sorption is suspected as the dominant attenuation mechanism. An example of such a problem is about the description of contaminant movement through aquifer systems, especially for the ionic species typical of inorganic contaminants (EPA, 2007).

The partition coefficient,  $K_d$  is the ratio of the quantity of adsorbate sorbed per unit mass of solid 'q'  $\mu\text{g/g}$  to the quantity of adsorbate remaining in solution 'c'  $\mu\text{g/mL}$  at equilibrium. Calculations of the rate of movement of As through an aquifer depend on knowing the  $K_d$ , or more particularly:

- The nature of the adsorption isotherm
- Partitioning changes with environmental conditions, with the assumption that the system is reversible and that, sorption is independent of the adsorbate concentration in the aqueous phase.

As stated earlier in the text, sorption isotherms have been widely used to describe and predict adsorption of a contaminant in soil and sediment systems (EPA, 2007). Commonly used are the Langmuir and Freundlich isotherms which quantitatively describe adsorption data and are used to more accurately model field observations (Dunnivant *et al.*, 1992; Kent *et al.*, 1995). Such models are however only empirical and extrapolation of results cannot be made outside of measured ranges (EPA, 2007).

Accordingly, empirical models provide a mathematical description of observed experimental data and often relate the use of hydrous ferric oxide as the dominant sorbing material. The Langmuir equation is expressed as:

$$q = \frac{bKC}{1+KC}$$

where,

q = The concentration of adsorbate on the solid

C = The concentration in solution

b = The maximum number of available sites for adsorption

K = A constant related to binding strength

The Langmuir equation can be rearranged to a linear form, by letting  $K_d = \frac{q}{c}$ , hence  $K_d = bK - Kq$  and therefore, demonstrated by a plot of  $K_d$  versus  $q$ , with a slope of  $-K$  and intercept of  $b$ . Sposito (1984) reports that it is not uncommon for the relationship between  $K_d$  and  $q$  to be convex to the  $q$  axis rather than linear. The Freundlich isotherm on the other hand, has the form;  $q = AC_i^\beta$  where  $A$  and  $\beta$  are adjustable parameters and  $\beta$  can have a value between 0 and 1. A plot of  $\log q$  vs.  $\log C$  would be a straight line with an intercept of  $\log A$  and slope of  $\beta$  (EPA, 2007). The  $\beta$  value indicates the strength of the adsorption capacity of the media.

The aim of this study is to develop an effective remediation strategy for reduction of As in water at the Obuasi mine based on sorption processes occurring between the aqueous and solid interface, hence the objectives were to establish:

- Arsenic degradation capacity of the decommissioned tailings dam environment and empirical model(s) to describe the degradation pattern
- Relevant equilibrium concentration range and time frame for As degradation by natural attenuation

## METHODOLOGY

**Geology, metallurgic activity and hydrogeology:** The Obuasi mine is situated within the Ashanti gold belt of Ghana. The area is underlain by Paleoproterozoic Birimian and Takwaian rocks. In Ghana, the Birimian is classified into a two-fold litho-stratigraphic system consisting of metavolcanic and metasedimentary groups with an overlying younger arenaceous and clastic Tarkwaian group. The Obuasi area is mostly dominated by the Birimian rocks. The rocks of the metavolcanic group are dominated by low-grade tholeiitic basalts with intercalated pyroclastic rocks as well as the minor andesitic and felsic flows and chemical sediments. The metasedimentary rocks comprise low-grade metamorphosed volcanoclastics, wackes and argillites, considered as partly contemporaneous with the volcanic group. The Birimian rocks are intruded by hornblende-rich granitoids known as the belt type that are closely associated with the volcanic rocks and mica-rich granitoids referred as basin type which tend to border the volcanic belt and are in the metasediment units (Leube *et al.*, 1990; Taylor *et al.*, 1992; Hirdes *et al.*, 1992).

Gold in the Ashanti belt occur as quartz reefs in the metasediments or vein or lode type deposits near or at

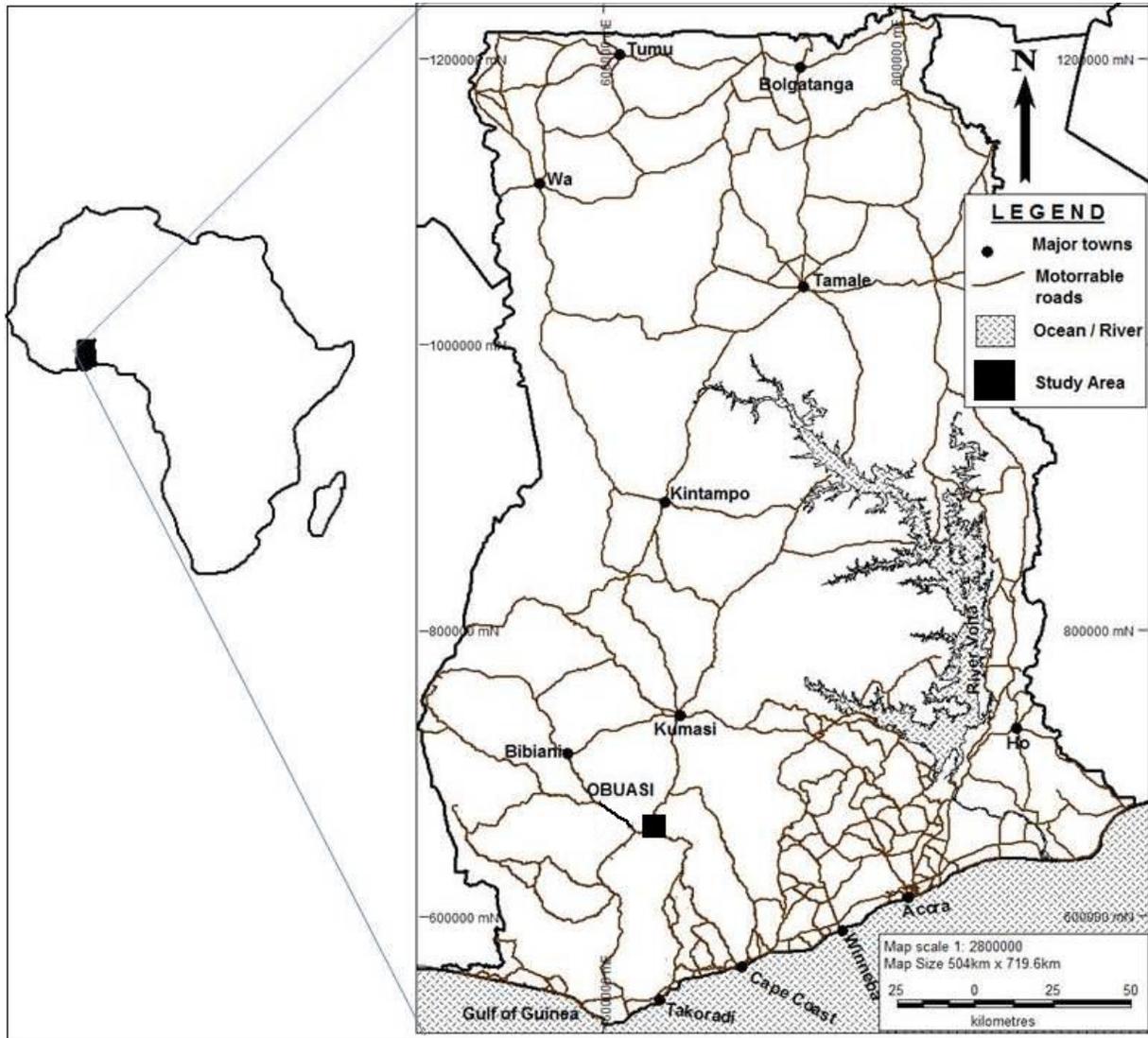


Fig. 1: Sketch Map of Ghana showing research location

the contact between the metasediments and metavolcanics (Kesse, 1985). The sulphide minerals in the ores are mainly dominated by the primary As bearing arsenopyrite (Osae *et al.*, 1995). Ore treatment using diversity of metallurgical methods (Marsden and House, 2006; Akcil and Ciftci, 2003) has been going on at the mine for over a century. Pyrometallurgical and hydrometallurgical pre-treatment methods as well as tailing retreatment were used to recover the gold over the years (Foli and Nude, 2012).

Geochemical activities in the sub-surface environment are influenced by water and water recharge fluctuations. In the Obuasi environment, stream flow volumes are usually large and turbulent with flow rates between 374 and 10,454 m<sup>3</sup>/h in the wet seasons. In the dry seasons, very low flow volumes that are at times made up of seepage from industrial sources flow at rates varying between 0 and 2,000 m<sup>3</sup>/h (Foli

and Nude, 2012). The top 30-80 m of the subsurface is made up of collapsible phyllitic and schistose material that marks the lower and upper limits of the water table (Foli, 2004). Porosities in this zone ranged from about 1.0-5.0×10<sup>-7</sup>m/s (Kumapley, 1993).

**Research location and climatic conditions:** Obuasi is located within latitude 5.35 and 5.65 N and longitude 6.35 and 6.90 N in the Ashanti Region of Ghana (Fig. 1). Climate is of the semi-equatorial type with double maxima rainfall regime. Mean annual rainfall ranges between 125 and 175 mm. Average annual temperature is 25.5°C. The vegetation is predominantly a degraded and semi-deciduous forest type (Obuasi Municipality, 2009).

**Fundamental requirements and initial site investigation:** Pre-monitoring site receptors to provide

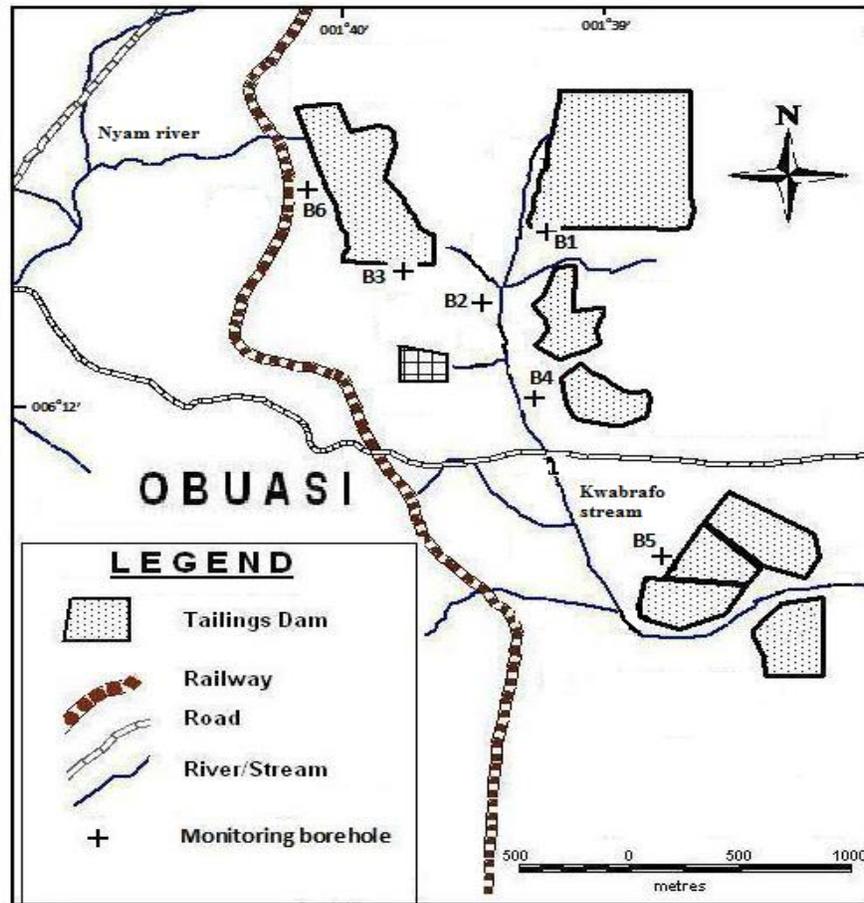


Fig. 2: Sketch map showing monitoring borehole locations

current or near-term receptor impacts are relevant for evaluation for possible pollution risk. Also, the local geologic and topographic maps, geologic data, geochemical data, contaminant concentration and distribution data are some good basis for assessing potential remedial approach to understanding the concept of As attenuation in the sub-surface. Other equally relevant requirements are borehole locations and spacing, stream profiles and sampling points, sampling and analysis plan etc. (Newell *et al.*, 2007).

Based on the hydro-geological settings of the area, actual and potential receptors of the COC are; well locations, tailings dam monitoring boreholes, seepages and surface water sources. Time-series contaminant source monitoring data made of historical records for As determinations from decommissioned dam sites are required for compilation, analysis and interpretation (Newell *et al.*, 2007).

**Water sampling and analysis:** Water monitoring sampling was done in tailings dam monitoring boreholes. In all, a total of 108 samples made up of 18 samples each from the six sites were taken over a period of 24 months; there were 6 missing data in the

collection due to seasonal factors (Foli *et al.*, 2012). Samples taken were therefore multiple within single sampling events. Results of the multiple samples were consolidated by averaging the values per sampling event for all 6 monitoring boreholes. Averaged results were therefore considered as one sample on each occasion (Newell *et al.*, 2007). Sampling map of the research work is presented in Fig. 2.

According to Newell *et al.* (2007), a minimum of four boreholes is adequate for measuring the COC per borehole, over at least six sampling events spread over the monitoring period, during which missing periods must not exceed two consecutive sampling periods. Also, a minimum of more than one year of quarterly monitoring was needed to establish a trend (ASTM, 2010). Sample numbers and sampling durations were in excess of minimum requirements, because of the need to obtain statistically meaningful correlation between the contaminant mass and time (Barcelona *et al.*, 1985, 1994; Azadpour-Keeley *et al.*, 2001). Samples were filtered with the arbitrary cut-off cellulose filter size of 0.45  $\mu\text{m}$ . Although 0.1  $\mu\text{m}$  pore size filters will generally provide a better assessment of results (EPA, 2007; Kim *et al.*, 1984; Hem and Robertson, 1967;

DeMora and Harrison, 1983), the 0.45µm filter size was adhered to in order to generate data in consonance with operational practices that depends only on rates of degradation. Detailed description of chemical and statistical analyses of the water samples are summarised in Foli and Nude (2012) and Foil *et al.* (2012), respectively. Being a natural attenuation program, detailed statistical evaluation of pertinent data was necessary in order to minimise the effect of natural seasonal variations of sampling and subsurface heterogeneity on groundwater quality (Gibbons, 1994; Gilbert, 1987; Hardin and Gilbert, 1993; McDonald and Erickson, 1994; O'Brien *et al.*, 1991; O'Brien, 1997).

clean plastic bag, tightly sealed. Sample site duplicates and sample blanks were taken for quality control analysis. Dynamic leaching method where leachant was replaced after each measurement was adopted. Distilled water of pH 6 containing, 3.0 ppm Al, 1.0 ppm Mn and 1.5 ppm Fe was used as leachant. Exactly 2 g of the sediment suspended in 100 mL leachant was stirred for 30 min and allowed to stand at room temperature. Samples of the leachant were extracted and filtered (Carboo and Serfo-Armah, 1997). In all, 14 sample extracts were analysed for As at time intervals of two-three weeks. The analysis was done using the Varian 55 B AAS device just as for water.

**Sediment sampling for leaching experiment and analysis:** Sediment samples were also taken from the vicinity of monitoring borehole sites, using an auger sampler at depths of about 30 cm. A well-cleaned plastic hand trowel was used to scoop the sediment samples. Samples were then mixed thoroughly to avoid biasing and thus make them representative of all the sites. About 200 g portion was then delivered into a

**RESULTS AND INTERPRETATIONS**

**Arsenic mass-time analysis:** Results of the monitoring in all 6 boreholes are presented in Table 1. Monitoring results from the multiple samples within single sampling events that were consolidated by averaging were labeled As<sub>1</sub>. The monitoring study established the concentration of As remaining in groundwater per unit

Table 1: Detailed monitoring data from boreholes

Time	BH	As									
1	1	<0.01	2	1	<0.01	3	1	0.19	4	1	<0.01
	2	<0.01		2	<0.01		2	<0.01		2	<0.01
	3	<0.01		3	<0.01		3	0.10		3	<0.01
	4	<0.01		4	<0.01		4	0.13		4	<0.01
	5	2.52		5	2.00		5	3.96		5	1.22
	6	<0.01		6	<0.01		6	0.27		6	<0.01
Mean		2.52			2.00			0.93			1.22
6	1	4.62	7	1	<0.01	9	1	<0.01	11	1	0.19
	2	0.55		2	<0.01		2	<0.01		2	<0.01
	3	0.45		3	<0.01		3	<0.01		3	0.10
	4	0.53		4	<0.01		4	0.97		4	0.13
	5	2.07		5	1.00		5	<0.01		5	2.96
	6	<0.01		6	<0.01		6	<0.01		6	0.27
Mean		1.64			1.00			0.97			0.73
12	1	0.18	14	1	<0.01	15	1	<0.01	17	1	0.3
	2	<0.01		2	<0.01		2	<0.01		2	0.07
	3	0.10		3	<0.01		3	<0.01		3	<0.01
	4	0.14		4	<0.01		4	<0.01		4	<0.01
	5	2.86		5	0.54		5	0.52		5	0.39
	6	0.26		6	<0.01		6	<0.01		6	0.47
Mean		0.71			0.54			0.52			0.31
18	1	0.12	19	1	<0.01	20	1	<0.01	21	1	0.37
	2	0.10		2	0.21		2	0.16		2	0.03
	3	0.05		3	<0.01		3	0.16		3	0.01
	4	0.54		4	<0.01		4	0.17		4	<0.01
	5	0.27		5	0.59		5	0.46		5	0.04
	6	<0.01		6	0.40		6	0.18		6	<0.01
Mean		0.22			0.40			0.23			0.11
23	1	0.14	24	1	<0.01						
	2	0.06		2	<0.01						
	3	0.04		3	<0.01						
	4	<0.01		4	0.15						
	5	0.06		5	<0.01						
	6	0.39		6	0.06						
Mean		0.14			0.11						

T: Time in months; BH: Borehole; as in (mg/L)

time. The leaching experiment also demonstrated the concentration of As leached into water per unit time and labeled As<sub>2</sub>. Both As<sub>1</sub> and As<sub>2</sub> results are presented in Table 2.

As summarized in Foil *et al.* (2012), the linear regression analysis of the borehole monitoring data indicated correlation between the arsenic concentration and time as 80% with statistical significance at 95% level of confidence. The spread of the data is between 0.45 and 1.135, while a *t-test* shows the model to be of significance at *p-value* of 0.000 (Table 3). The test therefore failed to reject the null hypothesis, establishing that there is a relationship between arsenic concentration and the months.

Concentration versus time plots, for both As<sub>1</sub> (field) and As<sub>2</sub> (experiment) data can be expressed by reducing mass balance in water and presented in Fig. 3.

From Fig. 3(A), equations for field monitoring (1; solid line) and also for experimental data (2; broken line) are exponential and represents adsorption and desorption data respectively. Model equations and R<sup>2</sup> values for both scenarios are presented below:

$$[As] = 2.520e^{-0.12t} \quad (R^2 = 0.913) \quad (1)$$

$$[As] = 778.7e^{-0.13t} \quad (R^2 = 0.847) \quad (2)$$

The above equations may be stated in the general form:

$$[As_n] = [As_0]e^{-m_e t_n} \quad (3)$$

From (3), [As<sub>n</sub>] is the concentration of As at any time *t<sub>n</sub>*, [As<sub>0</sub>] is the initial concentration of As and *m<sub>e</sub>* is the rate of degradation in the exponential function. Similarly, from Fig. (3B); equations for field (4; solid line) and experiment (5; broken line) are the linear equivalents of 1 and 2, respectively and with model equations and R<sup>2</sup> values as follows:

$$\log[As] = 0.401 - 0.053t \quad (R^2 = 0.913) \quad (4)$$

$$\log[As] = 2.891 - 0.056t \quad (R^2 = 0.847) \quad (5)$$

The general form of the above equations may also be stated as follows:

$$\log[As_n] = \log[As_0] - m_l t_n. \quad (6)$$

Table 2: Values of As per unit time in both monitoring (averages) and experimental values

Field monitoring		Experimental leaching	
Time in months	As <sub>1</sub> (mg/L)	Time in weeks	As <sub>2</sub> (mg/L)
1	2.52	1	970
2	2.00	2	-
3	0.93	3	-
4	1.22	4	130
5	-	5	-
6	1.64	6	350
7	1.00	7	-
8	-	8	200
9	0.97	9	-
10	-	10	270
11	0.73	11	-
12	0.71	12	360
13	-	13	-
14	0.54	14	150
15	0.52	15	-
16	-	16	120
17	0.31	17	-
18	0.22	18	80
19	0.40	19	-
20	0.23	20	80
21	0.11	21	-
22	-	22	60
23	0.14	23	-
24	0.11	24	-
-	-	25	20
-	-	26	-
-	-	27	20
-	-	28	-
-	-	29	-
-	-	30	10

From (6), *m<sub>l</sub>* is the slope of the line of best fit of the curve and is a factor of the rate of degradation in the linear function. The quantity *m<sub>l</sub>* is related to *m<sub>e</sub>* in (3) as, *m<sub>e</sub>* = 2.303 *m<sub>l</sub>*; and account for the concentration of As left in solution or leached out of sediment per unit time. This degradation rate may probably include all degradation pathways associated with mine sites. The R<sup>2</sup> values of 0.913 and 0.847 for both monitoring and experiment respectively, present very good predictive models. The significance of the R<sup>2</sup> values are that, 91.3% and 84.7% of the variance in the As concentrations from the monitoring and experimental processes can be attributed to the passing of time (EPA, 2004). Considering the number of data points used for the analyses, the R<sup>2</sup> values achieved a 99% level of significance. EPA (2004) indicated that, 10 data points with an R<sup>2</sup> value of 0.58 would be acceptable and would

Table 3: Model statistic of mass-time analysis for As in monitoring borehole

Source	SS	df	Ms	Number of obs = 18		
Model	6.35276473	1	6.352764730	F (1, 16)	= 62.700	
residual	1.62107971	16	0.101317482	Prob>F	= 0.0000	
Total	7.97384444	17	0.469049673	R-squared	= 0.7967	
				Adj R-squared	= 0.7840	
				Root MSE	= 0.3183	
As	Coef.	Std. Err.	t	p> t	(95% conf. interval)	
Moths_cons	-0.0811601	0.0102495	-7.92	0.000	-0.01028882	-0.0594321
	1.813455	0.1489613	12.17	0.000	1.497671	2.129239

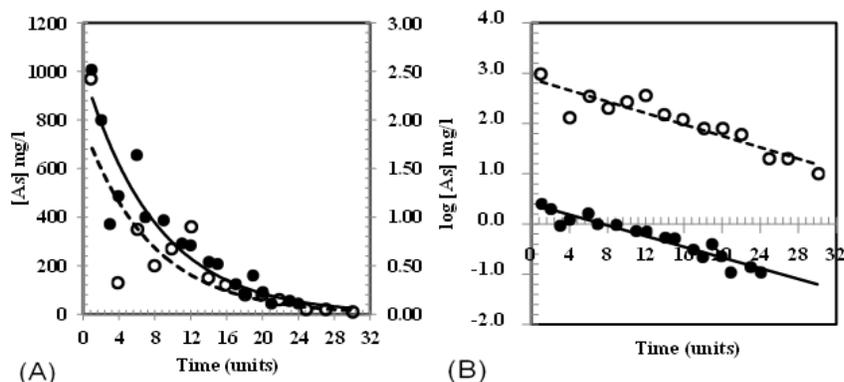


Fig. 3: (A) Exponential expressions with curves for monitoring (1; solid line) and experimental (2; broken line) data. (B) Linear expressions for monitoring (4: solid line) and experimental (5; broken line) data. Both sets of equations represent the concentration of As in water per unit time

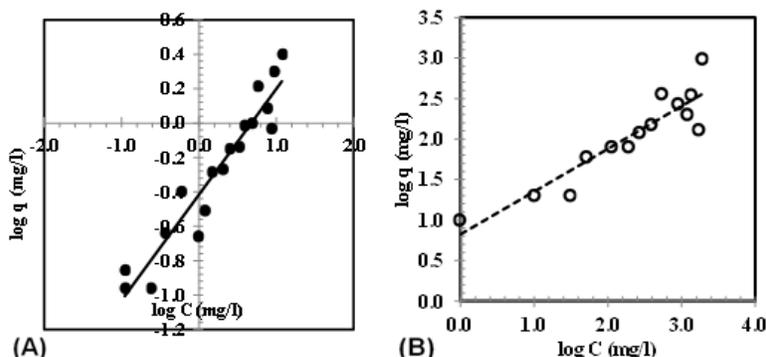


Fig. 4: Freundlich isotherm for As in monitoring (7) and experimental (8) data

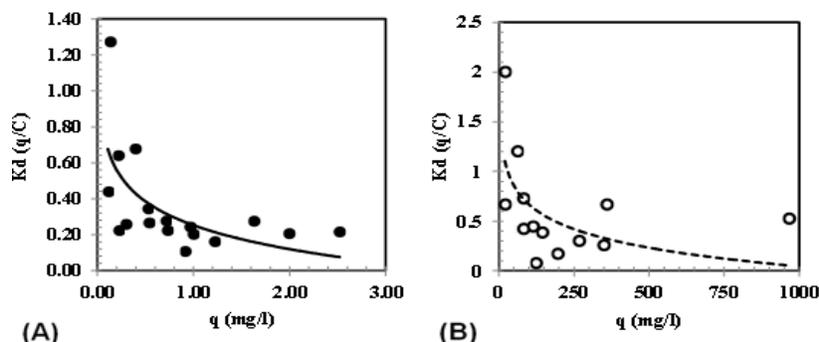


Fig. 5: Langmuir isotherm for As in monitoring (9) and experimental (10) data

be adequate for achieving 99% level of significance, thus confirming the sampling protocol outlined in Newell *et al.* (2007).

**Verification of sorption characteristics of As using relevant isotherms:** The Freundlich isotherm and the Langmuir isotherm were applied to both data to verify sorption processes. As stated earlier, the Freundlich Isotherm;  $q = AC_i^\beta$  may be re-stated as a log function of the form:  $\log q = \beta \log C + \log A$ , hence a plot of log

q vs. log C should be a straight line with an intercept of log A and slope of  $\beta$  (Fig. 4).

From Fig. 4, both the field monitoring data, as well as the experimental leaching data has model equations and  $R^2$  values respectively as follows:

$$\log q = 0.615 \log C - 0.415 \quad (R^2 = 0.912) \quad (7)$$

$$\log q = 0.528 \log C + 0.822 \quad (R^2 = 0.842) \quad (8)$$

Also, recalling the Langmuir equation can be re-arranged in the form:

$K_d = bK - Kq$ ; where,  $K_d = \frac{q}{C}$  and  $K_d$  is the partition or distribution coefficient. A plot of  $K_d$  versus  $q$  should therefore, be linear with a slope of  $-K$  and intercept of  $b$  (Fig. 5).

Despite the anticipated linearity, both model expressions in Fig. 5A and B above depict convex shapes between  $K_d$  and  $q$  to the  $q$  axis (e.g., Sposito, 1984). The model equations and  $R^2$  values for both field and experimental data, respectively are as follows:

$$y = -0.19 \ln(x) + 0.252 \dots (R^2 = 0.383) \quad (9)$$

$$y = -0.27 \ln(x) + 1.916 \dots (R^2 = 0.350) \quad (10)$$

Comparing the model equations in Fig. 4 and 5, it is clear from the high  $R^2$  values and the nature of the output curves from the Freundlich isotherm, as against those of the Langmuir equation makes the former a better predictive model than the latter. From Eq. (7 and 8), the gradients ( $\beta$ ) of the curve has values of 0.615 and 0.528 falling between 0-1 and therefore seem to suggest that adsorption process is a dominant process for the degradation of As (EPA, 2007). The Freundlich isotherm therefore provides clear empirical evidence that as reduction was governed by sorption processes and that, the validity of the estimated parameters only hold within the bounds of the data used (EPA, 2007).

**Arsenic mass-time analysis and environmental compliance:** Recalling the general Eq. (3 and 6); the relationship between the As concentrations ( $As_1$  and  $As_2$ ) and times ( $t_1$  and  $t_2$ ) from both monitoring and experimental data, respectively, can be calculated. The experimental data served as the test for model for the field monitoring data. The calculated time frames for both processes are based on highest concentration determined in monitoring (2.52 mg/L) and also on standard environmental compliance values (C), as

Table 4: Time estimates using sets of equations based Table 2

Monitoring (adsorption) data		Experimental (desorption) data	
C (mg/L)	(3A1/3B1) ( $t_1$ )	C (mg/L)	(3A2/3B2) ( $t_2$ )
2.52	0	0.01	-16
2.00	2	0.05	-28
1.00	8	0.10	-34
0.50	13	0.50	-46
0.10	26	1.00	-52
0.05	32	2.00	-57
0.01	45	2.52	-59

Explanation: Under equilibrium conditions; at  $t_1$ : 0, concentration adsorbed from water: 2.52 mg/L; At  $t_1$ : 45, concentration remaining in water: 0.01 mg/L; At  $t_2$ : 16, concentration desorbed into water: 0.01 mg/L; At  $t_2$ : 59, total desorbed concentration: 2.52 mg/L (-ve value indicates desorption)

published in Foli *et al.* (2012). The compliance values are 0.5 mg/L for livestock consumption (Wilson and Solomon, 2002), 0.10 mg/L for EPA standards value for mining effluent discharges into water bodies (EPA (GH), 1994), 0.05 mg/L for the primary maximum contamination level for drinking water (Wilson and Solomon, 2002) and 0.01 mg/L for WHO guideline value for drinking water (WHO, 2010). Also introduced to ensure uniformity is the arbitrary value of 2.00 mg/L, which may be a target value for any level of contaminant management. Substituting the compliance values in the model Eq. (3 or 6), we have corresponding time values  $t_1$  and  $t_2$  as presented in Table 4. A plot of  $t_1$  and  $t_2$  against compliance values and also  $t_1$  against  $t_2$  are also presented in Fig. 6A and B, respectively.

From Fig. 6A, model equations for monitoring (11; solid line) and experiment (12; broken line) data, as well as comparison between the two scenarios in 6B are presented as follows:

$$y = -8.19 \ln(x) + 7.566 \dots (R^2 = 1: \text{monitoring}) \quad (11)$$

$$y = 7.539 \ln(x) - 26.38 \dots (R^2 = 0.945: \text{experiment}) \quad (12)$$

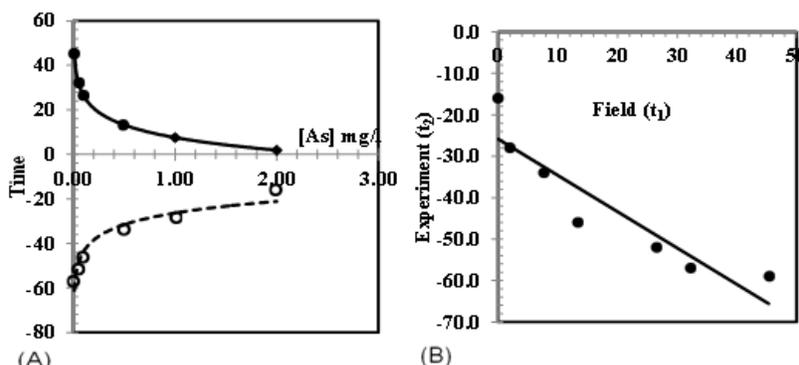


Fig. 6: (A) Adsorption of As from monitoring (11; solid line) and desorption (-ve) of As from experimental (12; broken line) data based on non-hypothesized range of compliance values. (B) Comparison between monitoring and experimental data

Table 5: Test of hypothesis of equality of  $t_1$  and  $t_2$  values

C	$t_1$	$t_2$	Mean (m)	$\Delta t_1 = (t_1 - t_m)$	$\Delta t_2 = (t_2 - t_m)$	$\Delta t$	
						$t_1$	$t_2$
2.52	0	59	29.5	-29.5	29.5	NA	0.5
2.00	2	57	29.5	-27.5	27.5	13.8	0.5
1.00	8	52	30.0	-22.0	22	2.8	0.4
0.50	13	16	14.6	-1.6	1.4	0.1	0.1
0.10	26	28	27.0	-1.0	1.0	0.0	0.0
0.05	32	34	33.0	-1.0	1.0	0.0	0.0
0.01	45	46	45.5	-0.5	0.5	0.0	0.0

Table 6: Time estimates after the non-equality hypothesis test on  $t_1$  and  $t_2$

Monitoring (adsorption) data		Experimental (desorption) data	
C (mg/L)	$(t_1)$	C (mg/L)	$(t_2)$
0.50	13	0.01	-16
0.10	26	0.05	-28
0.05	32	0.10	-34
0.01	45	0.50	-46

Table 7: Re-arranged time estimates in Table 5 and the mean model values

C (mg/L)	$(t_1)$	$(t_2)$	$(t_m)$
0.50	13	16	14.5
0.10	26	28	27.4
0.05	32	34	33.0
0.01	45	46	45.5

$$y = -0.877(x) - 25.85 \dots \dots \dots (R^2 = 0.850) \quad (13)$$

It can be observed from the  $R^2$  values in the model equations that the predictive models for both processes are not equal although they highly agree; as desorption (experiment) profile is slightly weaker than the adsorption (field) profile. Both  $t_1$  and  $t_2$  may then be statistically tested for equality of means using the t-test hypothesis to determine the range within which equilibrium can be attained.

**t-Test of hypotheses of means of  $t_1$  and  $t_2$ :** Comparing both  $t_1$  and  $t_2$  values listed in Table 4, by assuming the hypothesis for the equality of means for the paired t ( $t_1$  and  $t_2$ ) values corresponding to the concentration values of 2.52, 2.00, 1.00, 0.50, 0.10, 0.05 and 0.01 are not

equal; the test failed to reject hypothesis for the values 0.50, 0.10, 0.05 and 0.01, because of the very small and equal p-value as indicated in Table 5 and 6.

Within the limits of equality of  $t_1$  and  $t_2$  values (Table 6) and also as presented in Fig. 7,  $R^2$  values for both predictive models has been shown to be equal and absolute within the narrowed limit, of 0.05-0.01 mg/L and 14.5-45.5 months.

From Fig. 7, model Eq. (14 and 15), as well as comparison between the two scenarios in 16 are presented as follows:

$$y = -8.19 \ln(x) + 7.566 \dots \dots \dots (R^2 = 1: \text{Field}) \quad (14)$$

$$y = 7.75 \ln(x) - 10.55 \dots \dots \dots (R^2 = 1: \text{Experiment}) \quad (15)$$

$$y = -0.945 x - 3.399 \dots \dots \dots R^2 = 1 \quad (16)$$

The re-defined t values estimated above presented the exact limits of compliance value range within which both sorption processes progresses at equilibrium rate. Until this limit is attained, active methods of any sort may be used until the upper threshold limit is attained. Having established the range of compliance values for the rejection of the non-equality t values, thereby confirming equality of processes, desorption values can be negated to much up with the adsorption values and the mean values calculated as in Table 6 and 7 and Fig. 8 (same as in Fig. 7A).

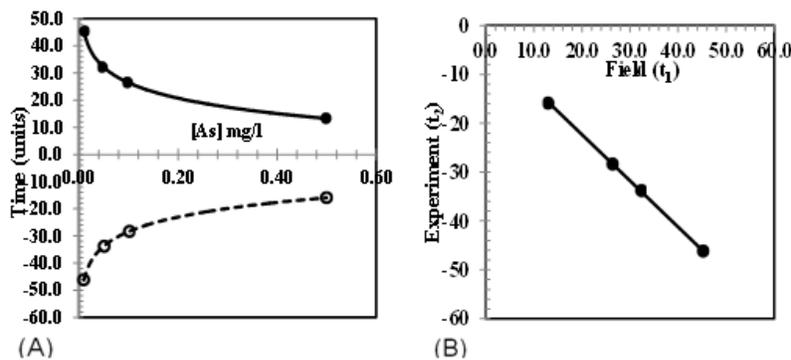


Fig. 7: (A) Adsorption of As from monitoring (solid line; 14) and desorption of As from experimental (broken line; 15) based on hypothesized range of compliance values. (B) Comparison between monitoring and experimental data.



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