

# Evaluation of an Integrated Approach Involving Chemical and Biological Processes for the Detoxification of Gold Tailings Effluent in Ghana

B. A. Osei<sup>1\*</sup> and R. M. Ahmed<sup>2</sup>

<sup>1</sup> *Department of Soil Science, School of Agriculture, University of Cape Coast, Cape Coast, Ghana*

<sup>2</sup> *Department of Agronomy, Faculty of Agriculture, University for Development Studies, Tamale, Ghana*

\*Corresponding author; E-mail: docbaosei@yahoo.co.uk

## Abstract

Chemical and bio-remediation measures for the detoxification of pollutants such as cyanide and heavy metals in mine tailings effluent have been developed over the years. The study sought to evaluate the decrease in the concentrations of Cu, Zn, Fe, Cd, As and Pb through the integration of the processes involving photo-oxidation, activated carbon, hydrogen peroxide and bacterial degradation to decontaminate wastewater from the gold ore treatment plant until release into the environment in Ghana. The levels of trace metals Cu (0.345 mg l<sup>-1</sup>), Zn (0.07 mg l<sup>-1</sup>) and Fe (0.146 mg l<sup>-1</sup>) in treated effluent released into natural water bodies after bacterial degradation was generally within international and local standards for effluent discharges. Except for As, the levels of Cd and Pb which are hazardous heavy metals that may pose adverse health and environmental effects were within acceptable limits. The toxicity of these metals were in the increasing order Pb < Cd < As. The anthropogenic source of As in the chemically processed arseno-pyritic rock ores of the study area and the marginal 14–49% efficiency of As of the different detoxification processes could have contributed to the high levels of As in the effluent. If optimal conditions are attained for the decontamination processes used, the multi-remediation approach could be an effective solution for the decontamination of mine tailings effluent.

## Introduction

Environmental pressure groups such as Wassa Association of Communities affected by Mining (WACAM), The National Coalition on Mining (NCOM) and Third World Network-Africa (TWN-Af) have expressed concerns over the magnitude of land degradation and water pollution that occur in mining environments in Ghana. In some mining communities, the spent rocks from surface mining operations deposited on agricultural lands deprive the people, who are predominantly farmers, of their livelihoods (WACAM, 2003). The heavy metals of sediments from waste dumps and deforested lands pollute rivers that serve as main sources of drinking water during heavy rainfall (NCOM, 2009; WACAM, 2003).

Arsenic concentrations up to 350 mg l<sup>-1</sup> have been reported to occur in stream waters affected by mining pollution in the Obuasi area of southern Ghana by Smedley (1996). Surface mining operations have resulted in stream pollution from cyanide spillages, acid mine drainage (AMD) and tailings leakages (Owusu-Kwateng, 2005). These activities have serious health implications and deprive the people in these communities access to the basic human need of good quality drinking water (Owusu-Kwateng, 2005; WACAM, 2008). The global economic and environmental climate has changed in recent years, and there is increasing pressure on mining companies to clean up toxic wastes and improve regulatory frameworks to attract foreign direct investment flows (OECD, 2002).

Several processes have been employed in the decontamination of effluent containing cyanide and associated heavy metals worldwide. These include natural degradation by ultraviolet radiation as in the tailings dam, oxidation by hydrogen peroxide ( $H_2O_2$ ), oxidation by chlorination, Cyanisorb process, the INCO process involving oxidation by  $SO_2$  (Akcil, 2003), Acidification-Volatilisation-Recovery (AVR) process, Acidification-Volatilisation-Neutralisation (AVN) process, sulphidisation, acidification, recycling and thickening (SART), conversion into stable iron cyanide precipitates and increased solution pH by liming (USEPA, 1994). However, an integration of different effluent detoxification methods is used by the mine under study, until final discharge into natural water bodies. These are the use of  $H_2O_2$ , carbon-in-solution (CIS), photo-oxidation and rotating biological Contractors (RBCs), that involve bacterial degradation with *Pseudomonas* sp. at different points of effluent flow (Opong, 2008).

Hydrogen peroxide oxidizes cyanide in solution, in the presence of the copper ion as a catalyst, to cyanate ion which, subsequently, hydrolyses to form ammonia and carbonate (Khodadadi *et al.*, 2005; Akcil, 2003). The  $H_2O_2$  process can be applied to waste waters but reagent requirements increase for slurries (USEPA, 1994). The photo-oxidative degradation of cyanide that occurs by UV radiation is slow but the rate of the reaction can be enhanced with increasing UV light intensity (Malhotra *et al.*, 2004) and, or in combination with  $H_2O_2$  (Malhotra, Pandit, Kapoor & Tyagi, 2004). Columns of activated carbon are utilized in the CIS process to precipitate heavy metals

and dissolved gold (Opong, 2008). The precipitation and, or microbial degradation of thiocyanate also occur in the activated carbon columns (Dictor *et al.*, 1997). The destruction of cyanide by bacteria results in the formation of ammonia, carbonates and sulphates from cyanide (Whitlock & Mudder, 1985; USEPA, 1994). The metal ions released from metal cyanides are sorbed and precipitated onto the biofilm of the rotating biological contractors, and the ammonia is finally converted into nitrate (Akcil, 2003; USEPA, 1994).

Bacterial degradation potentially provides a relatively cheaper and more efficient means of cyanide degradation than chemical methods (Akcil, 2003; Ebbs, 2004). Biological remediation and photolysis have an advantage over treatments such as the use of  $H_2O_2$  and activated carbon as in CIS, because thiocyanates are removed from waste waters (Akcil, 2003; Dash *et al.*, 2009). In biological treatment, free metals are either adsorbed within the biofilm or precipitated from solution (Dash *et al.*, 2009). The degradation of metals and metal cyanide complexes of Zn and Cu has been reported by Akcil (2003) and Botz (2001). An integration of chemical and biological treatments might, therefore, be a more appropriate approach to the detoxification of raw waste water produced from gold processing.

The specific objectives of this study were to assess the effectiveness of an integrated waste water detoxification regime, and to determine the extent of free cyanide and heavy metals decontamination of remediated tailings sites in a Ghanaian mining concession in relation to local and international acceptable thresholds.

#### Materials and methods

### *Site description*

The research was conducted within a Ghanaian mine, where the gold deposits occur along a zone of intensive shearing and faulting within the Precambrian greenstones. The mineral deposits are of two types, comprising of quartz veins containing high-grade free gold and the main sulphide ore in which narrow veins contain gold trapped within arsenopyrite. The soils of the area are classified as Ferralsols (FAO & IUSS, 2006). A main natural water body with some of its tributaries flow into and out of the mining concession.

### *Effluent flow and discharge into the environment*

The flow of effluent after gold extraction by the oxide and sulphide treatment plants, until discharged into the environment, is shown in Fig. 1. Briefly, the treatment of the processed gold ore effluent commences with its flow from the sulphide and oxide treatment plants into the tailings dam and also impoundments I and II (Fig. 1). Pond I, which was designed to flow into Pond II, is silted up and there are currently attempts to desilt it. The effluent in Pond II then flows into Pond III, which is treated with hydrogen peroxide to detoxify cyanide. Subsequently, the supernatant waste water from pond III and the holdings are recycled to the oxide and sulphide treatment plants for reuse. The supernatant waste water from the tailings dam is then channelled into the holdings pond.

The waste water in the holdings pond undergoes carbon-in-solution treatment in activated carbon columns and photo-oxidation treatments for the detoxification of heavy metals/removal of dissolved gold and cyanide, respectively. The process of bacterial degradation for the detoxification of cyanide, using *Pseudomonas* sp., then takes place via

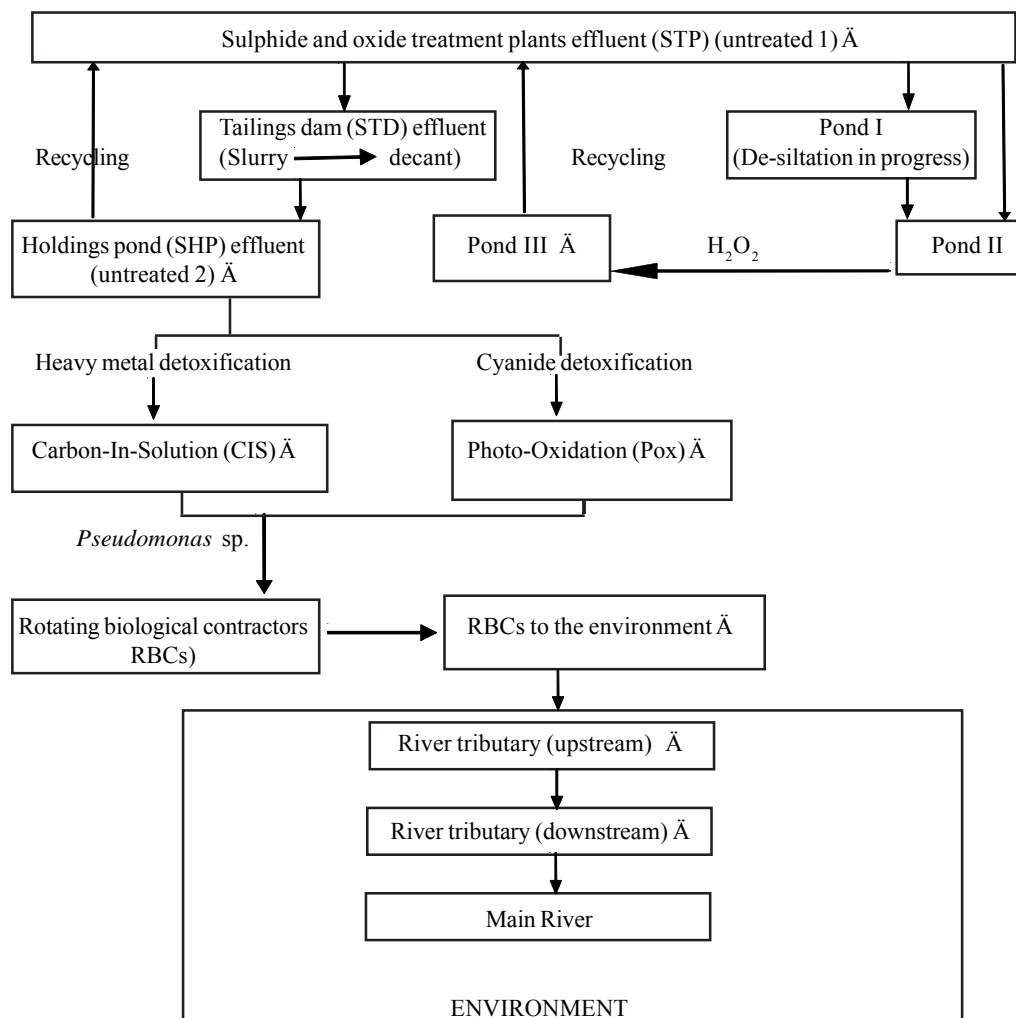
the Rotating Biological Contractors (RBCs). The resultant treated waste water is channelled into a fish pond and, subsequently, released into the water course of the environment. The treated effluent flows into the environment through the upper and lower courses into the main river which is a tributary of larger water bodies.

### *Effluent sampling and preparation*

The effluent of the study area was sampled and analysed. The effluent samples were taken in black 1-litre polyethylene bottles to minimize the degradation of cyanide by ultraviolet radiation. Samples were collected into the bottles after they had been initially rinsed with the effluent. Three grab samples were taken at different sampling points per effluent site. The oxidizing agent, chlorine, that can destroy cyanide in the effluent at the preservation stage, was neutralized by the addition of 0.06% ascorbic acid per litre of effluent. The samples were placed in an ice chest, at a temperature of about 4° C, from the field to the laboratory. The pH of the effluent was measured with the portable Yokogawa PH72pH/ORP pH metre. The pH of 50 ml of the subsamples to be analyzed for free cyanide were raised to 12 with NaOH solution to reduce losses due to volatilization of HCN and the transformation of CN<sup>-</sup> into stable cyanide compounds at low pH (Young & Jordan, 1995). The 50 ml subsamples for the analyses of heavy metals were acidified with concentrated HNO<sub>3</sub> (0.1% v/v) as a preservative (Chatterjee *et al.*, 1993).

### *Effluent analyses*

The concentrations of free cyanide (CN<sub>F</sub>), As, Pb, Fe and Zn of the tailings dam, holdings pond and detoxified effluent from processed gold ore were determined. Cadmium (Cd) and Cu, which form Weak



Ä Sampling points used for data analysis

Fig. 1. Flow chart of the detoxification of processed gold ore effluent

Acid Dissociable (WAD) metal-cyanide complexes, that readily dissociate to release toxic free cyanide, as well as the metal cations, were also determined. The analyses of the samples for free cyanide and heavy metal concentrations were conducted within 24 h and 1 week of sampling, respectively. The randomised complete block design with

three replications was used. The levels of free cyanide and heavy metals were also compared with local and international standards.

In the procedure used for cyanide determination a 10-ml test tube was filled with 6 ml of effluent sample. Effluent samples with free cyanide concentration,

more than the measurable maximum limit of  $5 \text{ mg l}^{-1}$ , as for the effluent of the tailings and holdings dams, were diluted with de-ionized water and the dilution factor of 20 noted. The cyanide ion reacts with chlorine in chloro-T-amine to form cyanogen chloride that reacts with pyridine to form cyano-1-pyridine. The cyano-1-pyridine then reacts with dimethyl-1, 3-barbituric acid to form a complex dye with a red-blue coloration, with intensity dependent on the concentration of cyanide.

With the aid of micro-spoons provided by a cyanide determination kit, 0.04 g of each of the reagents, Chloro-T-amine powder (CN-1A) and Dimethyl-1, 3 barbituric acid (CN-2A) were added in sequence to the cyanide contaminated effluent. Three drops of the reagent Pyridine (CN-3A) were then added to the contents of the test tube and shaken for 1 min. A period of 5 min was allowed for the reactions to complete and the comparator used to determine the free cyanide level in the effluent (AGCL, 2000).

The 50-ml effluent samples used for the determination of heavy metals were filtered through a  $0.45\text{-}\mu\text{m}$  filter paper. The filtrate was analyzed for As, Pb, Zn, Cu, Fe and Cd, using the Atomic Absorption Spectrometer (AAS, Spectr AA 220) with an air/acetylene flame.

#### *Statistical analysis*

The Genstat statistical package (Genstat, 2003) was used for the analysis of the data. The analysis of variance (ANOVA) was used to determine the effects of processed gold ore effluent detoxification method on the levels of free cyanide and the heavy metals, As, Pb, Zn, Fe, Cd and Cu. The least significant difference (LSD) was used for the separation of means at the 95% confidence level.

### **Results and discussion**

#### *Temperature, pH and free cyanide of untreated and treated effluent of the mine*

The results of the temperature, pH and free cyanide of the effluent produced in the study area that were analyzed are presented in Table 1. The pH of the treated effluent discharged ranged from 6.12 to 7.47. The pH values of the untreated effluent ranged from 7.59 to 8.98 and were significantly different ( $P < 0.05$ ) from those of the treated effluent (Table 1). Free cyanide, in the form of hydrocyanic gas, is released from tailings waste, which occurs in the form of tailings slurry or decant of waste water at pH values less than 8 (Young & Jordan, 1995). Cyanide volatilization rates increase further with decreasing pH (Young & Jordan, 1995). The pH of the untreated mine waste after gold extraction is, therefore, raised through the addition of calcium hypochlorite, before the release. This could account for the higher pH of the untreated waste water in contrast to the treated effluent. It is worth noting that the pH of the feed of untreated waste water need to be sufficiently increased to ensure a higher pH of the discharged waste into the tailings dam. The pH values could be adjusted to the value of 11 or higher so that the free cyanide will be hydrolyzed to produce aqueous hydrogen cyanide and not released as hydrocyanic acid (Young & Jordan, 1995).

The effluent pH of 6.12 after bacterial degradation was less ( $P < 0.05$ ) than the values obtained for photo-oxidation, carbon-in-solution and hydrogen peroxide treatments. A pH of less than 7 at a temperature of  $25 \text{ }^\circ\text{C}$  is favourable for hydrolysis of the cyanate ( $\text{OCN}^-$ ) produced after bio-oxidation into  $\text{HCO}_3^-$ ,  $\text{NH}_4^+$  and

TABLE 1  
Temperature, pH and free cyanide of effluent of the study area

Treatment	Effluent pH	Temperature (°C)	Free cyanide (mg l <sup>-1</sup> )
Sulphide treatment plant effluent (untreated 1)	7.73	30.60	5.67
Hydrogen peroxide	7.22	30.27	0.23
Tailings decant (untreated 2)	7.59	31.07	31.67
Photo-oxidation	6.82	31.70	1.00
Carbon-In-Solution	7.47	30.50	10.67
Rotating Biological Contractors (Bacterial degradation)	6.12	30.60	0.43
Environment (upstream)	6.95	29.87	0.001
Environment (downstream)	6.84	29.80	0.001
lsd (0.05)	0.05	0.26	2.53
Ghana EPA effluent discharge permissible maximum limit	6.0-9.0	29-30	0.20
IFC/ World Bank effluent guidelines	6.0-9.0	<3°C differential	0.10
WHO guidelines for drinking water quality (2008)	n.h.c. <sup>1</sup>	n.l. <sup>2</sup>	0.07 <sup>3</sup>

<sup>1</sup>Not of health concern at concentrations normally occurring in drinking water

<sup>2</sup>Not listed

<sup>3</sup>Total cyanide

OH<sup>-</sup> ions (Goldstein, 1976). This might explain why the lowest ( $P < 0.05$ ) effluent pH condition was created after the metabolism of cyanide by thin films of the bacteria *Pseudomonas* sp. on rotating biological contractors (RBCs).

The operating effluent pH of 7.22 for the hydrogen peroxide treatment might not have been optimal to yield the desired reaction rate for an efficient reduction of the total cyanide, and, subsequently, the free cyanide levels in the effluent. This is because the formation of HCN and its volatilization into the atmosphere is optimal at pH less than 9.7 (Khodadadi *et al.*, 2005). The pH value of 6.95 of the effluent discharged into the upstream water course was greater ( $P < 0.05$ ) than that of upstream water (6.84). Fluctuations occur in the pH of the effluent

discharged from the rotating biological contractors (RBCs) into the environment. The fluctuations in the pH of effluent discharged from the RBCs over time could have contributed to the higher ( $P < 0.05$ ) effluent pH of the water upstream. The soil of the mining area is acidic (pH of  $5.53 \pm 0.06$ ). The soil solution that seeps from the acidic soil of the study area into the water course could have led to increased hydrogen ion activity at the lower course.

The pH of drinking water is considered by the World Health Organization guidelines for drinking water quality to be of no health concern at levels normally found in drinking water (WHO, 2008). Nonetheless, compliance with the effluent discharge limits of 6.0–9.0 set by the Ghana Environmental Protection Agency (Ghana EPA) is of great

relevance. This could ensure that neither highly acidic nor too alkaline waste waters are released into water bodies. The pH of the discharged effluent is within the Ghana EPA standards, and the survival of the organisms that occur in the stream, into which it flows, may not be adversely affected.

Temperatures measured for the treated waste water were significantly different ( $P < 0.05$ ) from those of the untreated effluent. Generally, the temperatures of both the treated and untreated effluent varied by  $\pm 1.43$  °C units. The effluent of the photo-oxidation treatment for the remediation of cyanide yielded the highest ( $P < 0.05$ ) temperature of 31.70 °C. This could be ascribed to the greater exposure and absorption of energy from ultraviolet light to degrade the cyanide of the effluent enclosed in a relatively small reservoir (Malhotra *et al.*, 2004).

The free cyanide levels of the untreated effluent were significantly ( $P < 0.05$ ) different from the levels in the treated effluent (Table 1). The mean concentration of free cyanide in the treated waste water ranged from 0.23 mg l<sup>-1</sup> for the hydrogen peroxide treatment to 10.67 mg l<sup>-1</sup> for the carbon-in solution (CIS) treatment. The free cyanide concentration of the effluent of the RBCs discharged into the environment was 0.43 mg l<sup>-1</sup>, which was found to be above the effluent discharge limits set by the Ghana EPA.

The efficiencies of the free cyanide remediation technologies (percent decrease of the concentration of free cyanide) of the waste water were hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) (95.9%), CIS (66.3%), photo-oxidation (96.8%) and bacterial degradation (98.6%). The least and most efficient remediation technologies were the CIS and bacterial degradation, respectively.

The percent efficiency of free cyanide remediation attained using the H<sub>2</sub>O<sub>2</sub> could be improved. If the optimal H<sub>2</sub>O<sub>2</sub> concentration, temperature and an effluent feed with pH above 7.73 are maintained to yield a residual effluent cyanide of zero for the H<sub>2</sub>O<sub>2</sub> treatment, a 100% decrease in free cyanide levels could be achieved. A zero residual effluent has been attained at a pH of 9.7, H<sub>2</sub>O<sub>2</sub> concentration of 6.65 mg l<sup>-1</sup> and a temperature of 35 °C by Khodadadi *et al.*, (2005). The CIS treatment is mainly designed to reduce the levels of dissolved As, Pb, Cd, Zn, Fe and Cu in waste water before final discharge into the environment.

Thiocyanate (SCN<sup>-</sup>) is adsorped on the activated carbon that is utilized in the CIS treatment (Dictor *et al.*, 1997). The thiocyanate, which is a weak acid dissociable species, is degraded into NH<sub>4</sub><sup>+</sup>, then converted into NO<sub>2</sub><sup>-</sup> and, subsequently, transformed into NO<sub>3</sub><sup>-</sup> (Dictor *et al.*, 1997). This could have accounted for the reduction in the concentration of free cyanide for the CIS treatment. Bacterial degradation potentially provides a relatively cheaper and more efficient means of cyanide degradation than chemical methods (Akcil, 2003; Ebbs, 2004). The highest efficiency of the effluent detoxification after passing through the RBCs confirms the efficiency perspective of these findings.

#### *Water soluble As, Cd, Pb, Cu, Zn and Fe concentrations in untreated and detoxified effluent*

The data in Table 2 shows the concentrations of the dissolved heavy metals, As, Pb, Cd, Cu, Zn and Fe, in untreated and treated effluent, in mg l<sup>-1</sup>, at the study site.

#### *Detoxification of hazardous heavy metals (As, Pb and Cd)*

TABLE 2  
Heavy metal concentrations in effluent of the study area

Treatment	Dissolved metals (mg l <sup>-1</sup> )					
	As	Pb	Cd	Cu	Zn	Fe
Sulphide treatment plant effluent (untreated 1)	3.328	0.135	0.034	0.834	0.085	0.250
Hydrogen peroxide	1.700	0.101	0.029	0.352	0.052	0.213
Tailings decant (untreated 2)	5.043	0.177	0.034	2.049	0.124	0.182
Photo-oxidation	3.702	0.104	0.029	0.786	0.052	0.132
Carbon-In-Solution	4.234	0.110	0.018	0.440	0.044	0.125
Bacterial degradation	4.354	0.106	0.032	0.348	0.070	0.146
Environment (upstream)	0.949	0.044	0.020	0.026	0.049	0.164
Environment (downstream)	0.915	0.033	0.018	0.019	0.035	0.152
lsd (0.05)	0.086	0.008	0.002	0.047	0.010	0.012
Ghana EPA maximum permissible limit	0.20	0.10	-	2.0	2.0	2.0
IFC/WB effluent guidelines (2007)	0.10	0.20	0.05	0.30	0.50	2.0
WHO guidelines for drinking water quality (2008)	0.01	0.01	0.003	2.0	n.h.c*	n.h.c*

\*Not of health concern at concentrations normally occurring in drinking water

The levels of dissolved As, Pb and Cd in the treated wastewater were significantly lower ( $P < 0.05$ ) than those of the untreated wastewater (Table 2). The concentrations of the untreated effluent of the sulphide/oxide treatment plants (3.328 mg l<sup>-1</sup>) and the tailings decant (5.043 mg l<sup>-1</sup>) after the different detoxification treatments were in the ranges of As (1.7–4.354 mg l<sup>-1</sup>), Pb (0.101–0.110 mg l<sup>-1</sup>) and Cd (0.018–0.032 mg l<sup>-1</sup>) (Table 2). Subsequently, this yielded effluent that was discharged from the RBCs into the environment with levels of As and Pb that were 21.78 and 1.06 fold the effluent discharge limits set by the Ghana EPA. On the other hand, using the Environmental, Health and Safety (EHS) effluent guideline of the International Finance Corporation/World Bank (IFC/WB, 2007), an assessment of the quality of the discharged wastewater indicated that As, Pb and Cd concentrations

differed, respectively, by factors of 43.54, 0.53 and 0.64. The guideline values are more stringent for Pb than As for the IFC/WB (2007) standards and *vice versa* for the Ghana EPA (2006) limits.

Generally, except for As, the effluent concentrations of the metals under consideration are within acceptable limits. However, the trend of the toxicity of the effluent discharged into the environment based on these two standards decreased in the order As > Cd > Pb. An As concentration of 4.354 mg l<sup>-1</sup> in the discharged wastewater poses a potential risk to the surrounding environment. This could be through the contamination of groundwater and downstream water bodies used for irrigation (Liu, C.-p., *et al.*, 2010). The seepage of As, Pb and Cd into soil from the point of discharge could aggravate the environmental risks of farmers in the nearby communities.



The As, Pb and Cd concentrations in the water upstream were 78.2%, 58.5% and 37.5%, respectively, less than that of the effluent concentration discharged into the environment. The analytical data of the lower course of the stream showed greater decreases in the concentrations of As, Pb and Cd in the treated wastewater flowing into the environment by 79.0%, 63.6% and 43.8%, respectively. These significantly lower levels of the dissolved metals with distance along the water course could be partly ascribed to the dilution effect as has similarly been observed by Huang *et al.* (2008). A consideration of the WHO (2008) guidelines for drinking water quality implies that the natural water body into which the effluent is discharged could be considered as contaminated with As, Pb and Cd, if drunk by inhabitants of the surrounding communities.

However, it is worth noting that although the typical natural levels of As in fresh water is less than 0.01 mg l<sup>-1</sup> (Smedley & Kinniburgh, 2002) the levels of As in the water bodies, that flowed through upstream and downstream farming communities, were 0.949 mg l<sup>-1</sup> and 0.915 mg l<sup>-1</sup>, respectively. These values are also as much as 91.5–94.9% greater than the WHO (2008) guidelines for drinking water quality and could have harmful effects on human health if used as drinking water (Bhattacharya *et al.*, 2002). Of greater concern is the fact that the soluble and exchangeable fractions of toxic metals in soils are the most important associated to ground water pollution and to plant nutrition as noted by Sastre *et al.* (2001).

#### *Detoxification of trace metals (Zn, Cu and Fe)*

The separation of means indicated that there was a significant difference between the untreated and treated effluent at the 95% confidence level. All the different detoxification methods, therefore, decreased the levels of Zn, Cu and Fe, but to varied extents (Table 2). The percent decrease of the concentrations of the Zn, Cu and Fe for the different waste water remediation technologies were hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) (38.8%, 57.8% and 14.8%), CIS (64.5%, 78.5% and 31.3%), photo-oxidation (58.1%, 61.6% and 27.5%) and bacterial degradation (43.5%, 83.0% and 19.78%), respectively.

The percent reduction in the level of Cu was least for the H<sub>2</sub>O<sub>2</sub> treatment. This was possibly due to the use of Cu<sup>2+</sup> as a catalyst in the oxidation of cyanide solution by H<sub>2</sub>O<sub>2</sub> into CNO<sup>-</sup> which is subsequently hydrolyzed into CO<sub>3</sub><sup>2-</sup> and NH<sub>4</sub><sup>+</sup> (Akcil, 2003). The CIS process, which is mainly designed for the detoxification of heavy metals in wastewater, was the most effective treatment in reducing the levels of Zn and Fe. The CIS was more efficient in reducing the concentration of Cu in the wastewater, except for the bacterial degradation process. Moderate amounts of cyanide complexes of Cu and Zn are bio-degraded or bio-absorbed during bacterial treatment. In bacterial degradation, metal complexes of cyanides are converted into HCO<sub>3</sub><sup>-</sup> and NH<sub>3</sub>, while the freed metals are either precipitated from solutions or absorbed within the bio-film (Akcil, 2003). The reduction in the effluent concentration of Cu and Zn might, therefore, have been due to degradation, precipitation or adsorption onto the bio-film of the rotating biological contractors.

The levels of the dissolved Zn and Fe in raw and treated effluent were less than the

Ghana EPA standards (2006) (Table 2). The level of dissolved Cu in the untreated processed gold ore tailings decant was +0.049 mg l<sup>-1</sup> above the Ghana EPA maximum permissible level of 2.0 mg l<sup>-1</sup>. However, after treatment the Cu level in the effluent from the rotating biological contractors (RBCs) was decreased by 83% to comply with the Ghana EPA set limits before discharge into the environment. In compliance to the set standard, a concentration of 0.348 mg l<sup>-1</sup> was achieved at the point of discharge of the treated waste water into the environment (Table 2). The order of magnitude in the occurrence of dissolved metals was Cu > Fe > Zn in both the treated and untreated effluent. Generally, the levels of Zn, Cu and Fe in the treated effluent were below the WHO (2008) drinking water quality guidelines.

### Conclusion

The concentrations of free cyanide in the tailings mill effluent after treatment in the study decreased by more than 90% for the photo-oxidation, hydrogen peroxide and bacterial treatments. However, the levels of free cyanide released into the environment were 0.03 mg l<sup>-1</sup> and 0.13 mg l<sup>-1</sup> greater than the local (Ghana EPA, 2006) and international (IFC/WB, 2007) effluent discharge limits, respectively. The efficiency of free cyanide detoxification of the different remediation processes could be improved by ensuring optimal conditions of effluent pH, catalyst/reagent concentrations and increased bacterial degradation activities.

The carbon-in-solution (use of activated carbon), which is solely incorporated into the multiple detoxification chain to precipitate dissolved gold and heavy metals was the most

efficient in the reduction of the levels of Fe, Zn and Cd. It is necessary to create optimal conditions in the activated carbon columns to ensure a higher percentage decrease in the levels of As, Cu and Pb. The beneficiation of gold in the study area is from arseno-pyrite rock ores, which results in the release of high amounts of As, contained in the feed of tailings effluent. The high levels of As in the effluent discharges could be partly due to the low efficiency (14–49%) of As detoxification of the different effluent remediation processes employed.

However, the concentrations of Cu, Zn and Fe attained after the integration of the four tailings effluent detoxification processes were lower than the local and international set limits for effluent discharges. The levels of Cd and Pb released into the environment were also in compliance with the IFC/WB (2007) guidelines for effluent discharges. The incorporation of both chemical and biological processes could, therefore, have the potential to reduce the toxicity of gold mill effluent, if optimal conditions are created.

### Acknowledgement

The authors are grateful to the staff of the Environmental Department of AngloGold Ashanti, Obuasi mine, for their assistance in accessing the research sites and the analyses of the trace metals in their laboratory.

### References

- Akcil A. (2003). Destruction of cyanide in gold mill effluents: biological versus chemical treatments. *Biotechnol. Adv.* 21 (6): 501–511.
- Bhattacharya P., Jacks G., Ahmed K. M., Routh J. and Khan A. A. (2002). Arsenic in groundwater of the Bengal delta plain aquifers in Bangladesh. *Bull. envir. Contaminat. Toxicol.* 69: 538–545.
- Botz M. M. (2001). *Overview of Cyanide Treatment Methods*. Mining Environmental Management. Mining Journal Ltd., London. pp. 28–30.

- Chatterjee A., Das D. and Chakraborti D.** (1993). A study of groundwater contamination by arsenic in the residential area of Behala, Calcutta, due to industrial pollution. *Envir. Pollut.* **80**: 57–65.
- Dash R. R., Gaur A. and Balomajumder C.** (2009). Cyanide in industrial wastewaters and its removal: A review on biotreatment. *J. Hazard. Mater.* **163**: 1–11.
- Dictor M. -C., Battaglia-Brunet-Bayyaglia F., Morin D., Bories A. and Clarens M.** (1997). Biological treatment of gold ore cyanidation wastewater in fixed bed reactors. *Envir. Pollut.* **97** (3): 287–294.
- Ebbs S.** (2004). Biological degradation of cyanide compounds. *Curr. Opin. Biotechnol.* **15**: 231–236.
- Food and Agricultural Organization and International Union of Soil Sciences.** (2006). World Reference Base for Soil Resources. A Framework for International Classification, Correlation and Communication. *World Soil Resources Reports* **103**. FAO, Rome.
- Genstat** (2003). *Genstat Discovery Edition 3. In Genstat for Windows. Release 7.1. Introduction.* (R. W. Payne, eds.), pp. 193–231. Lawes Agricultural Trust (Rothamsted Experiment Station), VSN International Ltd., Oxford.
- Ghana Environmental Protection Agency (GEPA)** (2006). *Guidelines for Effluent Discharges into Natural Water Bodies. Maximum Permissible Levels.* Environmental Protection Agency, Accra, Ghana.
- Goldstein M.** (1976). Economics of treating cyanide wastes. *Poll. Engng.* **8**: 36–38.
- Huang X., Sillanpaa M., Duo B. and Gjessing E. T.** (2008). Water quality in the Tibetan plateau: metal contents of four selected rivers. *Envir. Pollut.* **156**: 270–277.
- International Finance Corporation and World Bank Group (IFC)** (2007). Performance Indicators and Monitoring. Environment. Emissions and Effluent Guidelines. *Environmental, Health and Safety Guidelines for Mining*. Washington DC. pp. 20–21.
- Khodadadi A., Abdolahi M. and Teimoury P.** (2005). Detoxification of Cyanide in Gold Processing Wastewater by Hydrogen Peroxide. *Iranian J. envir. Hlth Sci. Engng.* **2**(3): 177–182.
- Liu C.-p., Luo C.-l., Gao Y., Li F.-b., Lin L.-w., Wu C.-a. and Li X.-d.** (2010). Arsenic contamination and potential health risk implications at an abandoned tungsten mine, southern China. *Envir. Pollut.* **158**: 820–826.
- Ma L. Q. and Rao G. N.** (1997). Chemical fractionation of cadmium, copper, nickel and zinc in contaminated soils. *J. envir. Qual.* **13**: 372–376.
- Malhotra S., Pandit M., Kapoor J. C. and Tyagi D. K.** (2004). Photo-oxidation of cyanide in aqueous solution by the UV/H<sub>2</sub>O<sub>2</sub> process. *J. chem. Technol. Biotechnol.* **80** (1): 13–19.
- NCOM** (2009). *National Coalition on Mining (NCOM) Press Statement: Environmental Protection Agency Subverts Community Concerns.* Third World Network-Africa, Accra.
- Opong E. A.** (2008). *Biological Cyanide Detoxification - Laboratory, Pilot and Main Plants Updates.* AngloGold Ashanti, Obuasi Mine, Obuasi.
- Organization for Economic Cooperation and Development (OECD)** (2002). Environmental Impacts of Foreign Direct Investment in the Mining Sector in Sub-Saharan Africa. In *OECD Global Forum on International Investment. Conference on Foreign Direct Investment and the Environment.* (C. N. Boocock ed.), pp. 1–26. Paris, 7–8 February, 2002
- Owusu-Koranteng H.** (2005). *Presentation on the Social Impact of Gold Mining in Ghana – Unequal Distribution of Burdens and Benefits and its implications on Human Rights at the 11th EADI General Conference.* Retrieved November 2009, 11, from [www.wacamghana.com](http://www.wacamghana.com).
- Sastre I., Vicente M. A. and Lobo M. C.** (2001). Behavior of cadmium and nickel in a soil amended with sewage sludge. *Land Degrad. Dev.* **12**: 27–33.
- Smedley P. L.** (1996). Arsenic in rural groundwater in Ghana. *J. Afr. Eth Sci.* **22**(4): 549–470.
- Smedley P. L. and Kinniburgh D. G.** (2002). A review of the source, behaviour and distribution of arsenic in natural waters. *Appl. Geochem.* **217**: 517–568.
- Stolz J., Yang P. and Ambruster T.** (2000). Cd-exchanged heulandite: symmetry lowering and site preference. *Microp. Mesop. Mater.* **37**(1–2): 233–242.
- USEPA (United States Environmental Protection Agency)** (1994). *Treatment of Cyanide Heap Leaches and Tailings.* United States Environmental Protection Agency, Washington, D C. pp. 4–23.

- WACAM** (2003). *Fact Finding Mission (FFM) on Human Rights Abuses of Ashanti Goldfields Company (Obuasi Mine); The Case of Sansu Community*. (H. Owusu-Koranteng, ed.) Retrieved November 11, 2009, from [www.wacamghana.com](http://www.wacamghana.com): <http://www.wacamghana.com/app/webroot/img/documents/4af45f8961a48.pdf>
- WACAM** (2008). *Joint Statement by WACAM and Concerned Farmers Association of Teberebie on the Seepage of Cyanide Containment of AnglGold Ashanti Iduapriem mine*. Retrieved on November 12, 2009, from WASSA Association of Communities Affected by Mining at <http://www.wacam.com>
- Whilock, J. L. and Mudder, T. I.** (1985). The Homestake Wastewater Treatment Process: Biological Removal of Toxic Parameters from Cyanidation Wastewaters and Bioassay Effluent Evaluation. *Fundamental and Applied Biohydrometallurgy. Proceedings of the Sixth International Symposium on Biohydrometallurgy*. Vancouver, B. C., Canada. pp. 327–339.
- World Health Organisation (WHO)** (2004). *Guidelines for Drinking-water Quality, Vol. 1, Recommendations*, 3rd edn. Retrieved April 6, 2008, from [http://who.int/water\\_sanitation\\_health/dwq/GDWQ2004.web.pdf](http://who.int/water_sanitation_health/dwq/GDWQ2004.web.pdf).
- Young C. A. and Jordan T. S.** (1995). Cyanide remediation: Current and past technologies. In: *Proceedings of the 10th Annual Conference on Hazardous Waste Research*. (L. E. Erickson, D. L. Tillison, S. C. Grant and J. P. McDonald eds.), pp. 104–129, Manhattan, 23–24 May, 1995.