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Aerobic Bio-Precipitation of Heavy Metal Contaminated Dredged Materials from the Niger Delta

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Abstract: The abandonment of unconfined dredged materials in the Niger Delta following oil exploration is becoming a cause for concern because of the release of heavy metals during the natural weathering of sediments containing pyrites. During a laboratory scale bioremediation studies, *Acidithiobacillus* sp. was isolated from the spoil using 9 k media (10%) and used as inoculum in a controlled experiment for the leaching of two different abandoned dredged spoils (spoil 1 and 2) obtained from the mangrove forest of the Niger Delta. Results showed that the bacterium is able to catalyse the leaching of metals from the spoils into solution, with the following leaching efficiencies; Cu (92%), Cd (100%), Cr (50%), Ni (82%), Mn (80%) and Zn (92%) for spoil 1. Spoil 2 had similar leaching efficiencies. The mechanism of leaching involves the microbial oxidation of the pyrite in the dredged spoils resulting in pH decrease, which released the metals into solution due to changes in the redox chemistry of the leaching liquor. The study therefore have the potential of being applied in a large scale for the removal of heavy metals from dredged materials prior to their abandonment to prevent heavy metal pollution through natural weathering processes.

Key words: Acidification, *Acidithiobacillus* sp., bioremediation, bio-precipitation, dredging, oil exploration, Niger Delta, pyrite

INTRODUCTION

Oil exploration, which is the mainstay of the Nigerian economy accounted for over 90% of the country's export and 80% of her earnings. Most of the Nigeria's oil resources are located in the Niger Delta region. The Niger Delta is made up ecosystem that is dominated by the presence of wetlands and several creeks, creeklets and rivers that are relatively shallow, which made access to oil bearing location to be difficult by water craft. The coastal Niger Delta is also the route to Nigeria's offshore oil locations. Logistic support and supply for the offshore facilities is threatened. Also, the high siltation rate is compounding the access challenges and reinforcing the need for dredging. In order to overcome these access limitations, dredging is carried out.

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Dredging is one of the routine operations carried out by oil exploration companies when operating in wetlands. Dredging is necessary to create navigable accesses to facilitate routine operational activities such as drilling, pipeline construction and installation production of facilities etc and for the support of production logistics such as the transportation of oil production equipment and production crew exchange and also the supply of food to field workers. During dredging, waterway sediment, soil, creek banks and vegetation along the right of way are typically removed and because of lack of better ways to manage the concomitant dredged materials, they are deposited as spoils at the bank of the newly dredged canal (Ohimain, 2004). A number of impacts are associated with the abandonment of dredged materials especially in mangrove ecosystem in addition to the direct impact of the dredging activity itself. For instance, because the abandoned dredged materials are unconfined and uncapped, they are exposed to the high torrential rainfall exceeding 3000 mm per annum. These rains washes silt and sand from the spoil dump back into the canals and in addition to the high sediment deposition in the Niger Delta, create the need for remedial or maintenance dredging, which the oil industries called sweeping and the vicious cycle of dredging and sedimentation continues to the detriment of the ecosystem. The cycle of dredging and sedimentation often increase turbidity plumes causing alterations in the population of phytoplankton and zooplankton communities (Toumazis, 1995; Ohimain *et al*., 2002, 2004, 2005, 2008a).

Ohimain *et al.* (2008b) reported that though the impact of dredging is short term on water quality, but leachates from dredged materials containing pyrite have compounded and prolonged the impact arising from the dredging. Mangrove soil and sediment are regarded as sulphidic because of the presence of pyrite mineral. As long as pyrite remain in the sediment in the absence of air, they are innocuous, but their disturbance through dredging followed by oxidation, when they are disposed unconfined, leads to acidification (Ohimain, 2004) because of the oxidation of pyrite to sulphuric acid. Pyrite is common in the soil and sediments of the entire Gulf of Guinea, with a high presence in the Niger Delta (Sylla *et al*., 1996). Dredging has been reported to cause the re-suspension of sedimentary pyrites, which is linked to the re-mobilization of contaminants particularly heavy metals and increasing their bioavailability (Perin *et al*., 1997). Re-suspension of sediment causes the oxidation of sediment leading to the mobilization of metals into the water body (Saulnier and Mucci, 2000). The weathering sulphidic spoils often results in acidification and the release of heavy metals into the environment (Ohimain *et al*., 2008b). Mangrove ecosystem are known to fix heavy metals in their sediments (Ouyang *et al*., 2002; Stephens *et al*., 2001a, b; Delaune and Smith, 1985; Gambrell, 1994; Peterson *et al*., 1997), but the disturbance of the sediment through dredging and spoil disposal often change the redox chemistry of the ecosystem, which triggers pyrite oxidation and acid production through the activities of an acidophilic bacteria, *Acidithiobacillus* sp. using oxygen and ferric iron as catalysts (Ohimain, 2008). Obiajunwa *et al*. (2002) reported heavy metal pollution around hydrocarbon production facilities in the Niger Delta.

The release of heavy metals from abandoned dredged spoil is a major threat to environmental sustainability, thus militating against the realisation of Millennium Development Goal No. 7. Heavy metals are toxic even at low concentration, they cannot be biodegraded, but they bioaccumulate along the food chain. Kwon and Lee (1998) reported that heavy metals are toxic and exert chronic and lethal effects on aquatic animals and plants. Hence, the aim of this study is to isolate the acidophilic iron oxidising bacteria from the despoiled sites and use them as inoculum for the controlled leaching of contaminated spoils for the bioremediation of heavy metals.

MATERIALS AND METHODS

This study was carried out in a dredged canal (5°31"N, 5°31"E) leading off a tributary of the Warri River in the mangrove swamp of the Niger Delta about 20 km from Warri in Delta State, Southern Nigeria. The vegetation here is typical of mangrove swamp dominated by *Rhizophora* species. The area is characterized by high relative humidity (80-92%) and annual average rainfall exceeding 2800 mm. Although, there are two seasons (wet and dry), measurable precipitation occurs in all the months of the year. Notwithstanding, the period of April to October is often regarded as raining season, while November-March is regarded as dry season. Atmospheric temperature ranged between 27 to 29°C (Egborge, 1994).

Two different composite dredged spoil samples were collected in June 2000 namely spoil 1 (matured spoil i.e., about 5 years of abandonment) and spoil 2 (recent spoil i.e., <4 months of abandonment). The samples were air-dried at ambient conditions. They were pounded and sieved through 2 mm mesh and consequently preserved for further analysis. Result of laboratory analysis (Ohimain *et al*., 2008c) show that the spoils are contaminated by heavy metals (Table 1).

In order to isolate the mesophilic, chemolithotrophic, acidophilic bacteria of the genus *Acidithiobacillus*, 1 g of spoil sample was suspended in 100 mL each of 10% 9 K medium in Erlenmeyer (shake) flask. The composition of 9 K medium used was according to Silverman and Lundgren (1959) containing per litre: 3.0 g $[NH_4]_2SO_4$, 0.5 g K_2HPO_4, 0.5 g $MgSO_4$. $7H_2O$, 0.01 g $Ca[NO_3]_2$ and 0.10 g KCl. Water was added and made up to 700 mL. 1.0 mL of 10 N H_2SO_4 was added followed by 300 mL of 14.74% $FeSO_4$. $7H_2O$ and was adjusted to pH 3.5 using concentrated sulphuric acid. Nine K medium is a specialized medium for the isolation of iron oxidizing bacteria *Acidithiobacillus ferrooxidans* (Silverman and Lundgren, 1959). Each shake flask was plugged using cotton wool and incubated at 28±2°C for 4 weeks. The cultures were shaken for 1 h each day at 150 rpm (semi-static conditions). Growth was evident by increase in turbidity, color change of the media and microbial population increase. Cultures (10 mL) were transferred to fresh medium containing sterile spoils. This transfer continued until the population of active growing Acidithiobacilli was in the order of 10^6 MPN 100 mL^{-1}.

Ten grams each of spoils 1 and 2 were weighed into each of a 250 mL conical flask containing 100 mL of 9 k medium. The samples were sterilized at 121°C for 30 min. Each spoil was subjected to leaching processes using Acidithiobacilli inocula. A control set of samples was prepared without the addition of the bacteria. Eight pairs of media were prepared for the two spoil samples corresponding to Day 0, 7, 14, 21, 28, 35, 42 and 49. The cultures were incubated at 28±2°C in an incubator. Samples were collected weekly at each sampling day (0, 7, 14, 21, 28, 35, 42 and 49). Day 0 samples were collected after 30 min of incubation. Samples were analysed for microbial species, redox potential, pH, turbidity, optical density at 430 nm, ferrous iron, sulphate TDS and conductivity. The remaining samples were digested using $HNO_3/HClO_4/H_2SO_4$ for heavy metal analysis. Heavy metals were analysed using Buck

Table 1: Heavy metal composition of abandoned dredged spoils

Metal (mg kg^{-1})	Spoil 1	Spoil 2
Copper	93.30±0.26	121.1±0.30
Cadmium	122.0±2.00	130.8±0.53
Chromium	95.20±0.20	143.0±1.00
Nickel	93.00±0.20	138.5±0.36
Manganese	251.4±0.80	296.0±2.00
Zinc	118.1±0.78	131.5±0.50

Source: Oimain *et al.* (2008c)

Scientific 200A Atomic Absorption Spectrophotometer (AAS) for copper, cadmium, chromium, nickel, manganese and zinc (APHA, 1995). Redox potential and pH were analysed using a combination platinum/reference (Ag/Agcl) electrode (ATI Russel,) pH/Eh meter, turbidity was determined using Hach turbidimeter 2100P, TDS and conductivity with conductivity/TDS meter (Hach CO. 150), sulphate using turbidimetric method (Hach turbidimeter 2100P) and optical density (λ = 430 nm) using Hach 4000 Spectrophotometer. A correlation study was carried out among the parameters using SPSS version 11 and the significance of the correlation was determined at 0.05 and 0.01 probability levels (two tailed).

Metal recovery/leaching efficiency were calculated using the following equation (Seidel *et al*., 1998):

$$\text{Metal recovery (\%)} = \frac{\text{Metal content in leachate}}{\text{Initial metal content in dredged spoil}} \times 100$$

RESULTS

Earlier studies have shown that the abandoned dredged materials are rich in heavy metals (Table 1), with the metal content of spoil 1 being lower due to longer period of natural weathering and leaching processes (Ohimain *et al*., 2008c). During the controlled leaching experiment, pH declined continuously from the start of the experiment till the end (Fig. 1),

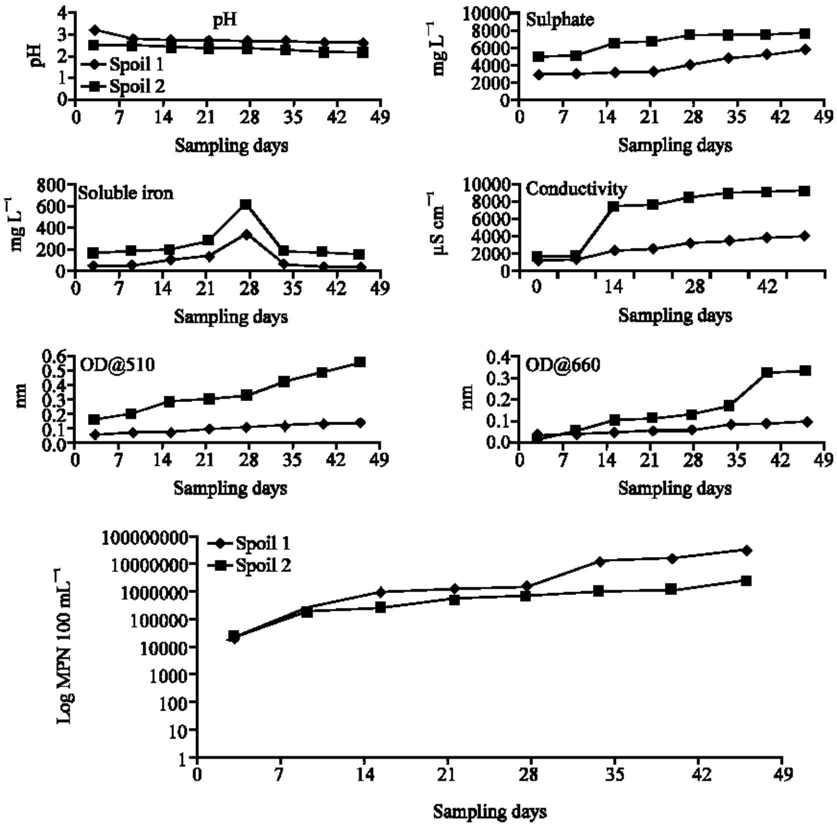

Fig. 1: Changes in selected microbial and physico-chemical parameters during bioleaching

Table 2: Pearson correlations coefficient of the monitoring parameters

Spoil 1	pH	OD@510	OD@660	Iron	Sulphate	Conductivity	Acidithiobacillus
pH	1	-0.907**	-0.878**	0.670	-0.938**	-0.880**	-0.840**
OD@510		1	0.979**	-0.905**	0.857**	0.708*	0.957**
OD@660			1	-0.883**	0.826*	0.691	0.983**
Iron				1	-0.586	-0.344	-0.899**
Sulphate					1	0.938	0.748*
Conductivity						1	0.614
Acidithiobacillus							1
Spoil 2	pH	OD@510	OD@660	Iron	Sulphate	Conductivity	Acidithiobacillus
pH	1	-0.960**	-0.949**	-0.070	-0.918**	-0.851**	-0.868**
OD@510		1	0.963**	0.110	0.983**	0.782*	0.837**
OD@660			1	-0.065	0.976**	0.715	0.914**
Iron				1	0.040	0.238	-0.158
Sulphate					1	0.699	0.841**
Conductity						1	0.523
Acidithiobacillus							1

*,**Correlation is significant at 0.05 and 0.01 level (2-tailed), respectively

Table 3: Visual observation during bioleaching of dredged spoil inoculated with Iron oxidizing bacteria using 10% 9 k medium

Sampling day	Observation	Deposition of orange brown precipitate[1]	Color of the leaching medium[2]	Turbidity[3]	Microbial slime[4]
0	Spoil 1	-	SB	+	-
	Spoil 2	-	SB	+	-
7	Spoil 1	-	GY	++	-
	Spoil 2	-	GY	++	-
14	Spoil 1	-	YY	++	+
	Spoil 2	-	YY	+++	+
21	Spoil 1	-	B	+++	+
	Spoil 2	-	B	+++	++
28	Spoil 1	+	B	+++	++
	Spoil 2	+	B	+++	++
35	Spoil 1	+	B	++	+++
	Spoil 2	+	B	++	++
42	Spoil 1	++	B	+++	+++
	Spoil 2	+	B	+++	+++
49	Spoil 1	+++	B	++++	+++
	Spoil 2	+	B	++++	+++

[1] Increasing precipitation; -: None, +: Low, ++: Moderate, +++: High. [2] Increasing color intensity; SB: Slightly brownish, GY: Greenish yellow, YY: Moderate yellow, B: Brownish. [3] Increasing turbidity; +: Low, ++: Moderate, +++: High; ++++: Very high. [4] Increasing slime production; -: None, +: Low, ++: Moderate, +++: High

indicating increasing acidity. Correlation analysis revealed that pH had an inverse relationship with virtually all the other parameters monitored (Table 2). The increasing acidity coincided with increase in the levels of other parameters including optical density, iron conductivity, sulphate and the population of *Acidithiobacillus* species. The pH strongly correlated inversely with optical density, sulphate, conductivity and bacteria population, which was significant at $\alpha<0.01$. Soluble iron increased from the beginning and attained peak concentration at day 28 and began to decline till the end of the experiment. Iron had a strong inversely relationship with optical density and bacteria at $\alpha<0.01$. As the leaching experiment progressed, the color of the leaching liquor changed from slight brown through greenish yellow, yellow and became brownish towards the end of the experiment. The precipitation of iron minerals (jarosites and other hydroxides of iron) began on the 28th day (Table 3). Turbidity increased as the population of the bacteria increased and microbial slimes became visible as from day 14 upwards (Table 3). Beside iron, other metals in the spoil matrix were leached into the liquor. At the end of the experiment, the percentage leaching of heavy metals were; Cu (92%), Cd (100%), Cr (50%), Ni (82%), Mn (80%) and Zn (92%) for spoil 1. Spoil 2 had similar leaching efficiencies (Fig. 2).

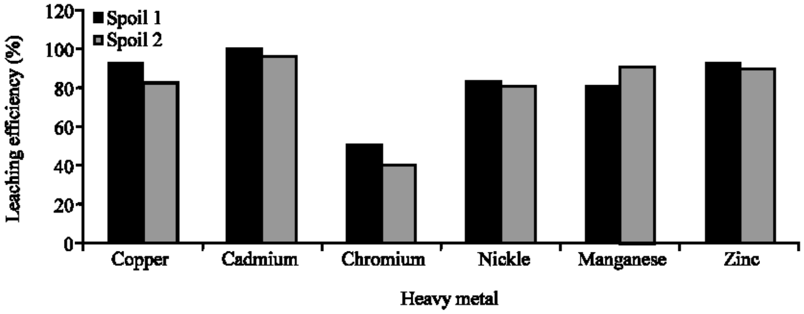

Fig. 2: Heavy metal leaching efficiency

DISCUSSION

It has been variously reported that the leaching of sedimentary pyrite result in the oxidation of pyrite to sulphuric acid (Rose and Cravotta, 1998; Ohimain *et al.*, 2004; Ohimain, 2004, 2008). During this study, pyrite oxidation coincided with increased concentration of sulphate and iron, while the population of acidophilic bacteria also increased. Iron had a strong inversely relationship with optical density and acidophilic bacteria at $\alpha = 0.01$. Soluble iron increased from the beginning and attained peak concentration at day 28 and began to decline till the end of the experiment. This unusual behaviour of iron may be as a result of precipitation of iron minerals (jarosites and other hydroxides of iron), which began on the 28th day (Table 3). Acidic drainage are usually formed by the oxidation of pyrite to release dissolved Fe^{2+}, SO_4^{2-} and H^+, followed by the further oxidation of the Fe^{2+} to Fe^{3+} and the precipitation of the iron as a hydroxide (Rose and Cravotta, 1998). Iron are known to be soluble at low pH, but with increasing oxidation of pyrite, ferric iron is formed, which precipitate out of solution, resulting in the decline of soluble iron (ferrous iron). Physical observations of the leaching liquor tend to support this assertion. As the leaching experiment progressed, the color of the leaching liquor changed from slight brown through greenish yellow, yellow and became brownish towards the end of the experiment. The various colors of the media relates to the changes in the speciation of iron in the media.

The increased acidity resulted in the leaching of the sedimentary heavy metals into solution. The percentage leaching of heavy metals were; Cu (92%), Cd (100%), Cr (50%), Ni (82%), Mn (80%) and Zn (92%) for spoil 1. This result was slightly higher than that of Seidel *et al.* (2003), who obtained the following results; Zn, Cd, Ni, Co and Mn were leached by up to 80%. Cu was partially dissolved, while Cr and Pb proved nearly immobile. Overall, they recorded 60-65% heavy metal removal within 6 weeks of leaching. Similarly, Wong *et al.* (2002) recorded the following efficiencies after 16 days of bioleaching; 50.2-78.4% of Cr, 63.7-74.1% of Cu, 74.9- 88.2% of Zn and 15.5-38.6% of Ni. Reasons for the differences in leaching efficiencies are due to the pH of the leaching media, redox changes, metal speciation, the solubility constants of the different metal and the diversity, activities and population of the acidophilic microorganisms in the leaching liquor and the initial concentration of elemental sulphur in the leaching media (Lovley and Coates, 1997).

CONCLUSION

The study was carried out on abandoned dredged spoils that are undergoing natural weathering and leaching heavy metals into the environment. The bacteria catalysing the oxidation of pyrite in nature, *Acidithiobacillus* sp. was isolated using 9 k media (10%) and used in a controlled laboratory experiment for the leaching of abandoned dredged spoils obtained from the mangrove forest of the Niger Delta. Results showed that the bacterium is able to catalyse the leaching of metals from the spoils into solution. The study therefore have the potential of being applied in a large scale for the removal of heavy metals from dredged materials prior to their abandonment to prevent heavy metal pollution through natural weathering process.

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