Journal of Scientific Research & Reports

21(3): 1-11, 2018; Article no.JSRR.45675
ISSN: 2320-0227

Removal of Heavy Metals In Spent Synthetic-Based Drilling Mud Using Nano Zero-Valent Iron (nZVI)

Obinduka Felix[1], Ify L. Nwaogazie[2*], Onyewuchi Akaranta[3] and Gideon O. Abu[4]

[1]Centre for Occupational Health, Safety and Engineering, University of Port-Harcourt, Nigeria.
[2]Department of Civil and Environment Engineering, University of Port-Harcourt, Nigeria.
[3]Centre of Excellence, Centre for Oilfield Chemicals Research, University of Port Harcourt, Port Harcourt, Nigeria.
[4]Department of Microbiology, University of Port Harcourt, Port Harcourt, Nigeria.

Authors' contributions

This work was carried out in collaboration between all authors. Author OF designed the study and wrote the protocol which was approved by his supervisors, Professors ILN, OA and GOA equally collected field samples and carried out laboratory analyses. Prof. ILN guided the statistical analysis and the draft report. Professors OA and GOA guided the laboratory studies. All authors read and approved the finial manuscript.

Article Information

DOI: 10.9734/JSRR/2018/45675
Editor(s):
(1) Dr. Farzaneh Mohamadpour, Department of Organic Chemistry, University of Sistan and Baluchestan, Iran.
(2) Dr. Shahid Naseem, Professor, Department of Geology, University of Karachi, Pakistan.
Reviewers:
(1) Julian Cruz-Olivares, Autonomous University of State of Mexico, Mexico.
(2) K. Kazeem, Salam, Ladoke Akintola University of Technology, Nigeria.
Complete Peer review History: http://www.sciencedomain.org/review-history/27742

Original Research Article

Received 23 September 2018
Accepted 01 December 2018
Published 15 December 2018

ABSTRACT

Management of waste generated from oil and gas activities in the Niger Delta, is a major environmental challenge given that if the spent mud is disposed without proper treatment, the heavy metals will pose a lot of health risks to human through ingestion or inhalation. The heavy metals are also toxic to marine organisms, if disposed into the sea, untreated. Spent synthetic drilling mud is a major waste stream, among its components, are heavy metals. Samples collected on day 0 and biweekly were digested and analysed using the atomic absorption spectrometer (AAS). With nano Zero-Valent Iron, nZVI, concentration of 0.75mg/L of the spent mud, more than 95% removal were recorded for most metals in 6 weeks and over 99% in 12 weeks. The residual heavy metal concentrations met global limits for effluent disposal. Mathematical models with the goodness of fit, R^2 of 0.999, were developed to predict the removal process.

**Corresponding author: E-mail: ifynwaogazie@yahoo.com, ifylnwaogazie@ipsng.org, ify.nwaogazie@cohseuniport.com;*

Keywords: Spent synthetic-based drilling mud; Niger Delta; heavy metals; Nano zero-valent Iron; mathematical model.

1. INTRODUCTION

Drilling and production operations are the two major activities of the upstream petroleum industry that produce a wide range of wastes that potentially impact the environment [1-5]. In these activities, two main types of waste are generated, drill cuttings and spent drilling mud. Drilling fluids including synthetic base fluids (SBFs) are the suspension of solid in liquid emulsion and/or dissolved materials with chemical additives which play significant roles during drilling. In synthetic mud, the base fluid is a synthetic oil which is highly degradable, a quality not possessed by Oil Based Mud (OBM) synthesised with crude oil. Additionally, SBM, possess other qualities of Oil-Based Mud (OBM) ,but more environmentally friendly .Drilling fluids provide relatively better shale inhibition, cool and lubricate the drill bit and drill strings and provide thermal stablity characteristics. Other functions include lifting of drill cuttings from the well, controlling the hydraulic pressure to prevent blowouts, and keeping the drilled well from collapsing before casing installation.

However, after drilling, the treatment and disposal of the spent mud becomes a major challenge especially when reconditioning, recycling or storage are no longer economically feasible. Improper disposal of spent drilling mud on land, can increase the soil acidity and damage the vegetation.Humans stand a high risk of ingesting the heavy metals through the food chain.Untreated spent mud,disposed on water,is toxic to marine organisms [6-8].

Heavy metals are some of the major contaminants in impacted spent drilling mud, that cause harm and pollution to the environment. The use of nano Zero-Valent Iron (nZVI) in treating soil and underground water containing heavy metals has been documented [9-13]. nZVI transforms the heavy metals to non or less toxic compounds. Several treatment options have been used to treat drilling waste of heavy metals, with some level of success. For instance, biosorption, whereby micro-organisms are used to adsorb the heavy metals, is being practiced [14]. However, being a natural process, biosorption, could be slow. This study is aimed at developing a cost effective and environmentally friendly method of treating synthetic-based mud of heavy metals, in a containment before disposal.

A highly reactive, remediation grade nZVI, manufactured by OnMaterials, Inc , Los Angeles, USA , was employed in this study to treat spent drilling mud of heavy metals. nZVI is cost effective and provides the most in consideration of reactivity and longevity in comparison to chemical oxidants. It does not contain harmful chemicals and is safer to handle when compared to chemical oxidants. They are sustainable, recycleable and green. nZVI interaction with heavy metals, being an abiotic reaction destroys contaminants with no toxic end products or by-products, and are free of rust and dust.

Samples of spent drilling mud from five oil fields in Niger Delta were treated with nZVI and tested bi-weekly for six weeks for heavy metal removal and results recorded. Control samples were also tested. This low cost method of treating spent mud will minimise indiscriminate dumping of the waste and reduce environmental pollution.

2. METHODOLOGY

2.1 Study Area

This study was carried out with spent drilling mud obtained from five oilfields in the Niger Delta. Niger Delta is located at an elevation of 96m above mean sea level. It lies between Longitude 5^o and 8^o East and Latitude 3^o and 6^o North. Samples A, B, C, D and E were taken at Longitude 5°9'40.58" East and Latitude 5°19'17.71" North, Longitude 6°47'4.91" East and Latitude 3°11'37.64" North, Longitude 6°16'41.97" East and Latitude 4°11'42.95" North, Longitude 6°21'20.38" East and Latitude 4°54'28.65" North, Longitude 6°42'12.08" East and Latitude 4°59'30.06" North, respectively (See Fig. 1).

The region has a population of 30 million people [15]. Over 90% of Nigeria's proven oil and gas reserves are domiciled in the region. The Delta covers a coastline of 560km^2, and it is formed primarily by sediment deposition. It's a rich mangrove swamp covering over 20,000km^2 within wetlands of 70,000km^2 [16,17].

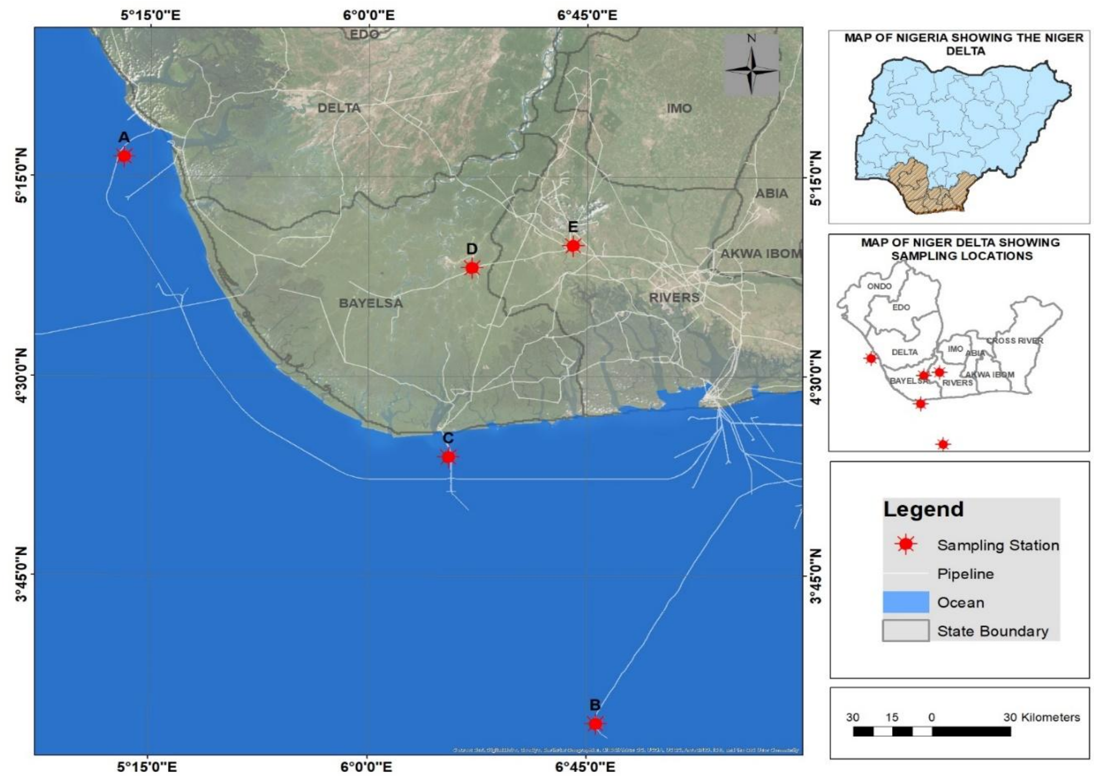

Fig. 1. Location map of study area

Oil was first discovered in the delta by shell-BP in 1957 at Oloibiri and production began in 1958. Oil and gas industry plays an important role in Nigeria's economy accounting for about 90% of its gross earnings. Fig. 1 shows the map of Niger Delta and spent drilling mud sample locations amongst other features.

2.2 Data Collection

Adequate quantities of the spent mud from the five oil fields were sampled from well agitated mud tanks and transported to the laboratory in less than 24 hrs. To ensure that the parameters of the mud did not change before testing. In the laboratory, the samples were again thoroughly agitated with 30 litre planetary mixer, for 30 mins, at the speed of 239 rpm, to ensure proper mixing. The samples were marked MUD-A to E. For each field, adequate quantities of the spent mud were transferred into 25 different containers. Each container was filled with 20 Litres of the mud. One sample was tested for baseline values of the physicochemical parameters. Six samples were set aside for control while 5, 10, and 15 g of nZVI were added to six samples each.

The temperature and pH of the samples were tested in line with ASTM-E2251-14 and ASTM D1293-15 respectively. Ambient temperature and neutral pH were recorded during the test. Control sample was the original spent mud without treatment The amended samples were thoroughly mixed for effective chemical reaction. To evaluate the effectiveness of nano-Zero-Valent Iron in the treatment of heavy metals encountered in spent drilling mud, 4 digested samples, one from 5, 10 and 15 g treatment , and control were tested by Atomic Absorption Spectrometer (AAS,PinAAcle 900H model). for the concentration of residual heavy metals ,every two weeks for twelve weeks and results recorded, Sample concentration was determined by comparing absorbance with that of standard. The same experiment was carried out simultaneously for MUD-B, MUD-C, MUD-D and MUD-E.

2.3 Predictive Model

Linear multiple regression analyses were applied in modelling the duration of effective removal of heavy metals from the spent drilling mud. XLSTAT 2016 was the statistical tool employed as an aid for the model development [18,19]. The data for the resultant reduction of the heavy metals for the various doses of treatment with nZVI for 12 weeks were used for modelling. The model was verified by using the data generated from the laboratory plotted against the predicted values.

3. RESULTS AND DISCUSSION

3.1 Results

Baseline concentration of heavy metals

Part of the samples collected from the field were analysed to establish the existing initial concentrations of the heavy metals and this is what is termed baseline data The initial concentrations of a total of seven heavy metals as well as pH and temperature are presented in Table 1. The maximum allowable values for effluent land disposal for Nigeria, some countries and United States Environmental Protection Agency (US EPA), are shown in Table 2.

Heavy Metal removal

Control Sample

The result of control sample (no treatment) is shown in Fig. 2.

The results of heavy metal treatment of sample-A with 5g, 10g and 15g of nZVI, at near neutral pH and ambient temperatures are presented in Figs. 3, 4 and 5, respectively.

Rate of heavy metal removal by 5, 10 and 15g doses of nZVI

The rate of mercury removal in the spent mud, using 5, 10 and 15g doses of nZVI is shown in Fig. 6. It can be seen from Fig. 6 that for the period of treatment, 15g nZVI treatment proved to be more effective than 5 and 10 g treatments. The same trend was observed with other metals.

Model for the prediction of residual heavy metals in impacted spent drilling mud using 5g, 10g and 15g of nZVI treatment

The average of the collected data for the experiments (MUD-A to E) with 5g nZVI are presented in Table 3.

Table 4 shows a summary of regression power modeling of Hg treatment using 5g nZVI. The 4th order polynomial model is the best model with respect to R^2, Mean Square Error, MSE and Root Mean Square Error, RMSE values.

A repetition of regression power modeling was carried out for the other heavy metals, based on R^2, MSE and RMSE values. The resultant model equations for heavy metal removal in spent synthetic based mud using 5g, 10g and 15g nZVI are presented in Table 5.

3.2 Discussion

Heavy metal Concentration in Impacted Media (Spent Drilling Mud)

The baseline results of the spent drilling mud (Table 1), show that most of the heavy metals exceeded the maximum allowable limits for effluent disposal on land according to the Department of Petroleum Resources (DPR) [19], the regulatory body in Nigeria, some selected countries, and US EPA [20] as shown in Table 2. Zinc concentration is in the range of 15.3 to 98.6mg/L while Chromium concentration is 17.3 to 60.2mg/L. Copper and Arsenic concentration are 10.4 to 26.5mg/L and 5.8 to 94.3mg/L, respectively. Mercury is present in the range of 1.3-2.29mg/L while Cadmium concentration is 0.037 to 6.2mg/L. Nickel and Vanadium are present in negligible concentrations. The pH is in the neutral range of 7.3 to 7.9. Temperature is ambient (28-29^{o}C).

The high level of heavy metals in the spent mud is capable of impacting on human health and the environment, if disposed on land untreated [21-24]. This means that the spent mud has to be treated before disposal.

Residual heavy metals

The five samples of the spent drilling mud studied had different levels of concentration of the heavy metals, most of which were above allowable limits by regulatory authorities (Table 2). However, after separate treatment with 5g, 10g and 15g of nZVI for 12 weeks, the concentration of the heavy metals dropped remarkably. A sharp drop was recorded in 4 weeks, after which the contaminant reduction continued progressively (Figs. 3 to 5). The ability of Iron as Fe(0) and Fe(II) to reduce redox sensitive elements has been demonstrated at both laboratory scale and field tests [10,25-29].

Table 1. Baseline distribution of heavy metals, pH and temperature of the spent drilling mud

		Sample designation				
S/NO	**Parameters**	**A**	**B**	**C**	**D**	**E**
1	pH	7.5± 0.01^b	7.3±0.01^a	7.8±0.00^c	7.4±0.09^a	7.9±0.00^c
2	Temperature (^{o}C)	28±0.00^a	28.3±0.10^b	28.7±0.05^c	29.0±0.00^d	28.5±0.10^{bc}
3	Pb (mg/L)	39.0±0.00^c	52.2±0.2^e	5.6±0.2^a	18.6±0.3^b	38.6±1.4^c
4	Zn (mg/L)	59.2±0.8^b	79.3±0.3^c	15.35±0.45^a	98.6±0.2^d	80.2±0.2^c
5	Cr (mg/L)	59.0±0.4^d	60.2±0.1^e	17.3±0.3^c	23.4±0.4^b	39.2±0.2^c
6	Cu (mg/L)	10.4±0.4^a	22.9±0.0^d	26.5±0.3^e	17.4±0.4^c	15.0±0.3^b
7	As (mg/L)	94.3±0.3^e	56.1±0.1^d	8.7±0.2^b	5.8±0.2^a	9.8±0.2^c
8	Hg (mg/L)	0.005± 0.001^a	1.70±0.25^{bc}	2.29±0.03^c	1.9±0.3^{bc}	1.3±0.2^b
9	Cd (mg/L)	0.037± 0.002^a	0.039±0.003^a	6.2±0.2^d	5.2±0.4^c	2.7±0.3^b
10	Ni (mg/L)	0.00±0.00^a	0.045±0.0025^b	0.001±0.00^{ab}	0.001^{ab}±0.00^{ab}	0.00±0.00^a
11	V (mg/L)	0.005±0.001^b	0.008±0.001^b	0.003±0.001^{ab}	0.003±0.001^{ab}	0.004±0.001^a

$^{a-e}$Results are presented as mean ± standard error. Means with different superscript, the homogenous subset of means, (a, ab, b, bc, c, d and e) within the same rows indicate significant differences ($p < 0.05$),

Table 2. Nigeria (DPR), some countries, and US EPA guidelines and standards for heavy metals on land

	Heavy metals (mg/L)						
Country	**As**	**Pb**	**Hg**	**Cd**	**Cr(VI)**	**Cu**	**Zn**
Bulgaria	100.0	26.0	0.03	0.4	65.0	34.0	88.0
Argentina	0.5	10.0	0.20	0.2	8.0	-	-
Tanzania	1.0	200.0	2.00	1.0	100.0	200.0	150.0
South Africa	58.0	20.0	0.93	7.5	6.5	16.0	240.0
Nigeria [19]	5.0	5.0	0.20	1.0	5.0	0.05	50.0
US EPA [20]	10.0	1.3	0.90	0.2	11.4	5.20	66.6

Source: [30,31]

Table 3. Average results of heavy metal removal using 5g of nZVI

	Heavy metal (mg/L)						
Time(week)	**Hg**	**Cd**	**Pb**	**Zn**	**Cr**	**Cu**	**As**
0	1.85	4.70	30.60	60.4	39.82	19.93	34.94
2	1.25	2.94	19.84	39.96	24.76	13.27	24.04
4	0.86	2.11	12.34	24.76	15.16	9.00	17.06
6	0.63	1.26	7.80	14.36	8.88	5.80	11.96
8	0.42	0.84	4.90	8.90	5.84	4.10	8.21
10	0.28	0.54	3.12	5.36	3.54	2.77	5.76
12	0.21	0.31	2.22	3.24	2.19	1.80	4.01

Table 4. Summary of regression power modeling of Hg using 5g nZVI treatment

Model type	**Equation**	**R^2**	**MSE**	**RMSE**
Exponential	$Hg = 1.80e^{-0.183t}$	0.9986	0	0.018
Polynomial				
2nd order	$Hg = 0.117t^2 - 0.2711t + 1.8024$	0.9948	0.003	0.052
3rd order	$Hg = -0.0008t^3 + 0.0261t^2 - 0.335t + 1.8407$	0.999	0.001	0.027
± 4th order	$Hg = 0.0001t^4 - 0.0038t^3 + 0.0484t^2 - 0.3857t + 1.85$	0.9999	0	0.012
5th order	$Hg = 5E\text{-}06t^5 - 3E\text{-}05t^4 -0.0022t^3 + 0.0415t^2 - 0.3761t + 1.8506$	0.9999	0	0.017
6th order	$Hg = -1E05t^6 + 0.0004t^5 - 0.0055t^4 + 0.0323t^3 - 0.0565t^2 - 0.2783t + 1.85$	1		

± *The best model with respect to R^2, Mean Square Error, MSE and Root Mean Square Error, RMSE values*

Table 5. Model equations for heavy metal removal in spent synthetic based mud using 5g, 10g and 15g nZVI

Heavy metal	Model type	Model equation	R^2	MSE
5g nZVI application				
Hg	4th order Polynomial	$0.0001t^4 - 0.0038t^3 + 0.0484t^2 - 0.3857t + 1.85$	0.9999	0.000
Cd	5th order Polynomial	$- 0.0001t^5 + 0.0047t^4 -0.055t^3 + 0.3238t^2 - 1.3282t + 4.6966$	0.9993	0.011
Pb	5th order Polynomial	$0.0002t^5 - 0.0047t^4 + 0283t^3 + 0.3568t^2 - 6.181t + 30.603$	1.0000	0.006
Zn	5th order Polynomial	$0.0003t^5 - 0.0091t^4 + 0.0928t^3 + 0.2874t^2 - 11.061t + 60.39$	1.0000	0.096
Cr	Exponential	$39.692e^{-0.242t}$	0.9996	0.048
Cu	3rd order Polynomial	$- 0.0095t^3 + 0.308t^2 - 3.8403t + 19.9$	0.9998	0.022
As	5th order Polynomial	$- 0.0003t^5 + 0.0093t^4 -0.1272t^3 + 1.0253t^2 - 7.0617t + 34.94$	1.0000	0.000
10g nZVI application				
Hg	5th order Polynomial	$-0.0002t^5 + 0.0058t^4 - 0.0803t^3 + 0.5379t^2 - 1.9537t + 4.16$	1.0000	0.000
Cd	5th order Polynomial	$-0.003t^5 + 0.0105t^4 - 0.1266t^3 + 0.7064t^2 - 2.1532t + 4.6951$	0.9986	0.022
Pb	Exponential	$30.60e^{-0.28t}$	1.0000	0.005
Zn	5th order Polynomial	$-0.003t^5 + 0.0139t^4 - 0.2832t^3 + 3.2218t^2 - 21.28t + 66.412$	1.0000	0.057
Cr	Exponential	$19.93e^{-0.312t}$	1.0000	0.002
Cu	4th order Polynomial	$0.0006t^4 - 0.0289t^3 + 0.5317t^2 - 4.8907t + 19.938$	1.0000	0.004
As	5th order Polynomial	$-0.002t^5 + 0.0064t^4 - 0.1057t^3 + 1.0863t^2 - 8.1829t + 34.941$	1.0000	0.001
15g nZVI application				
Hg	4th order Polynomial	$7E\text{-}05t^4 - 0.0033t^3 + 0.0588t^2 - 0.5031t + 1.8494$	1.0000	0.000
Cd	5th order Polynomial	$- 7E\text{-}05t^5 + 0.0026t^4 - 0.0404t^3 + 0.3438t^2 - 1.7608t + 4.7001$	1.0000	0.000
Pb	5th order Polynomial	$- 0.0002t^5 + 0.0102t^4 - 0.1821t^3 + 1.8193t^2 - 10.739t + 30.6$	1.0000	0.000
Zn	5th order Polynomial	$- 0.001t^5 + 0.0411t^4 - 0.678t^3 + 5.923t^2 - 28.938t + 66.418$	1.0000	0.006
Cr	Exponential	$19.93e^{-0.407t}$	0.9999	0.004
Cu	5th order Polynomial	$- 0.0003t^5 + 0.0097t^4 - 0.1409t^3 + 1.1776t^2 - 6.5369t + 19.928$	1.0000	0.004
As	Exponential	$34.94e^{-0.278t}$	1.0000	0.004

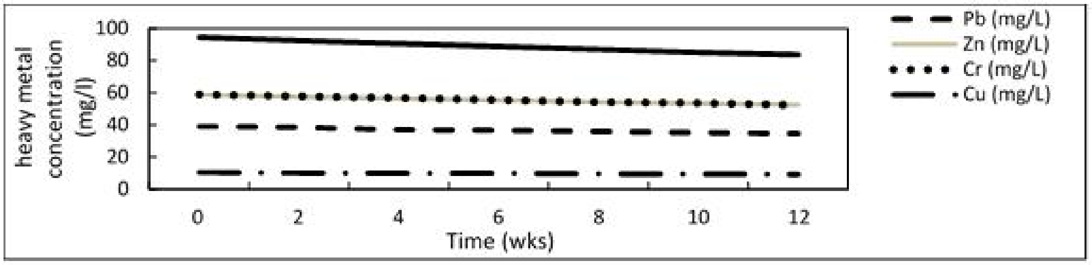

Fig. 2. Distribution of heavy metal reduction of control Sample-A

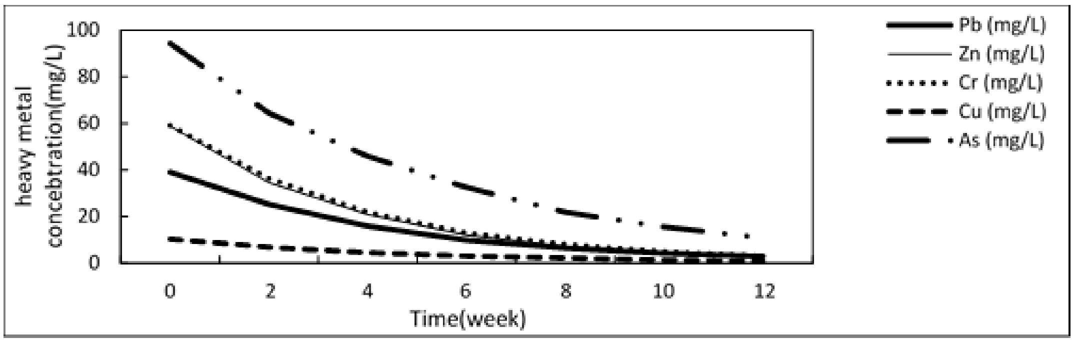

Fig. 3. Treatment response distribution of Sample-A with 5g nZVI

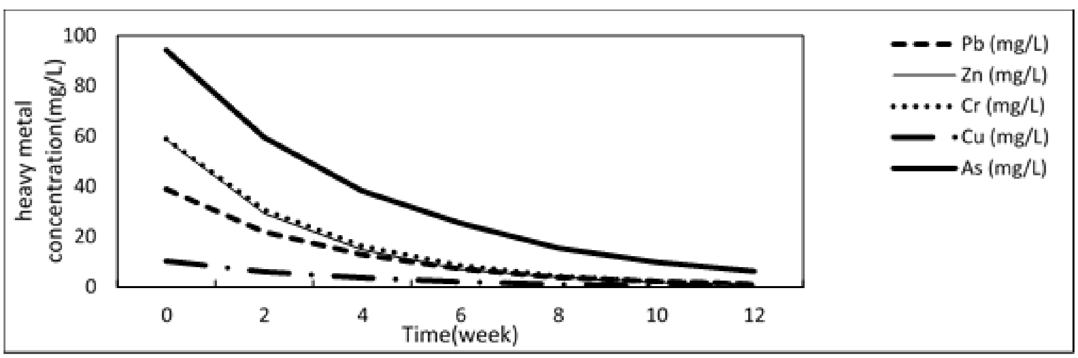

Fig. 4. Treatment response distribution of Sample-A with 10g nZVI

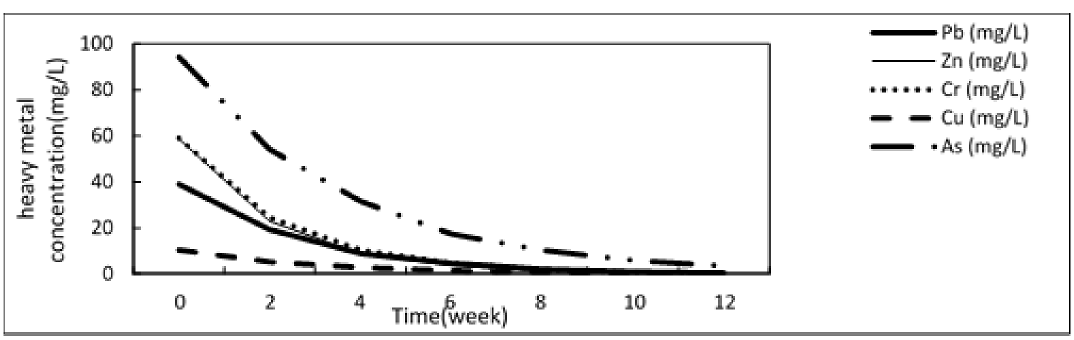

Fig. 5. Treatment response distribution of Sample-A with 15g nZVI

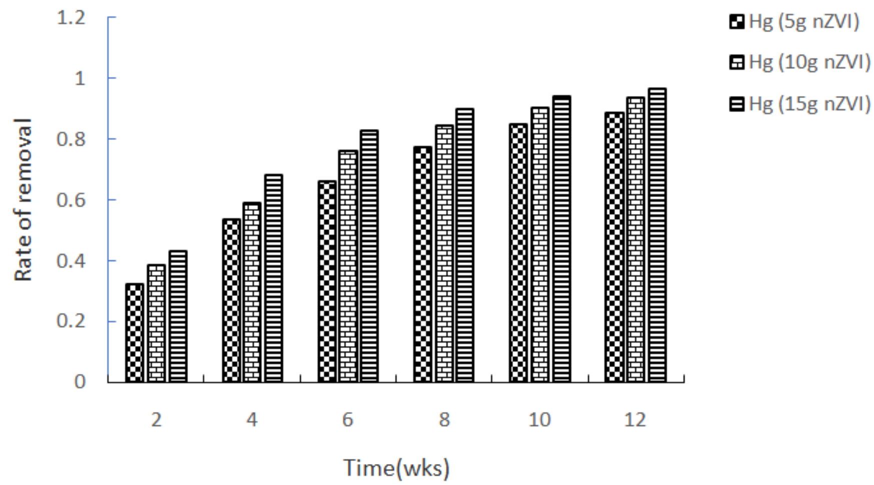

Fig. 6. Rate of mercury removal by 5,10 and 15 g treatments

Rate of heavy metal removal by 5, 10 and 15g doses of nZVI

The concentration of heavy metals in the spent drilling mud was brought down to 90%, 95% and 99% by 5, 10 and 15g nZVI treatments, respectively in twelve weeks (Figure 6). Iron based technologies for remediation of contaminated groundwater and soil has been documented [20,32,33,34]. nZVI has been proven to be a strong chemical reductant and is able to convert many mobile oxidised oxyanions e.g $CrO^2{}_4$ and oxycations e.g $UO_2{}^{2+}$ into immobile forms [35].

Control Sample

The control sample showed slight reduction in concentration of the heavy metals as can be seen in Fig. 1. This little reduction could be attributed to biosorption by some microorganisms like *Bacillus thuringiensis, Geomyces pannorum, Pseudomonas* sp., *Citrobacter* sp., etc. [36-39].

Nonlinear Regression Equations

Nonlinear regression equations developed for heavy metal treatment with 5g, 15g and 20g of nano Zero-Valent Iron show high goodness of fit, R^2 of 0.999 generally. With these models, it will no longer be necessary to repeat all the experiments in the chemical treatment of spent drilling mud with nZVI. Once the parameters in the model equations are established, the model can be used to predict the residual concentration of the heavy metal at any time, to a high accuracy. This will show when the attenuation process would be completed and save a lot of time and resources in the treatment of spent drilling mud using this method.

4. CONCLUSION

Based on this study, it can be concluded that spent drilling mud from different fields in the Niger Delta have different concentrations of heavy metals, and nZVI can effectively treat spent synthetic based mud laden with heavy metals. A reduction of over 99% in 12 weeks was recorded. The heavy metal concentrations in the treated spent mud, for the five mud samples tested complied with Nigerian DPR and other international prescribed limits (Table 2). Regression models of exponential and higher order polynomials can predict with high accuracy, the residual concentration of heavy metals in the spent drilling mud, at any point in time, using nZVI.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

REFERENCES

1. Ekundayo JA, Benka-Coker MO. Effects of exposure of aquatic snails to sublethal concentrations of waste drilling fluid. Environmental Monitoring and Assessment. 1994;30:291-297.

2. Bamberger M, Oswald RE. Impacts of gas drilling on human and animal health. New Solut. 2012;22:51–77.
3. Ferrar KJ, Kriesky J, Christen CL, Marshall, LP, Malone SL, Sharma RK, Michanowicz DR, Goldstein BD. Assessment and longitudinal analysis of health impacts and stressors perceived to result from unconventional shale gas development in the Marcellus Shale region. Int. J. Occup. Environ. Health. 2013;19:104–112.
4. Steinzor N, Subra W, Sumi L. Investigating links between shale gas development and health impacts through a community survey project in Pennsylvania. New Solut. 2013;23:55–83.
5. Vengosh A, Jackson RB, Warner N, Darrah TH, Kondash A. Acritical review of the risks to water resources from unconventional shale gas development and hydraulic fracturing in the United States. Environmental Science & Technology. 2014;48(15):8334–8348.
6. Levesque HM, Moon TW, Campbell PG, Hontela A. Seasonal variations in carbohydrate and lipid metabolism of yellow perch (*Perca flavescens*) chemically exposed to metals in the field. Aquatic Toxicology. 2002;60(3-4):257-267.
7. Dwived GK. Upadhyay SK, Mishra AK. Singh AK. Hyper accumulation of cadmium in *Solanum nigrum* L. and their effects on phyto-chemicals and antioxidant enzymatic activities. International Journal of Pharmaceutical Sciences and Research. 2014;5:1424-1430.
8. Mallmann FJK, Rheinheimer DS, Ceretta CA, Cella C, Minella JPG. Guma RL, Filipovic V, Oort F, Simunek J. Soil tillage to reduce surface metal contamination-model development and simulations of zinc and copper concentration profiles in a pig slurry-amended soil. Agriculture. Ecosystems and Environment. 2014; 196:59-68.
9. Li X, Elliot WL, Zhang W. Zero-Valent iron nanoparticles for abatement of environmental pollutants: Materials and engineering aspects. Critical Reviews in Solid State and Material Science. 2006;31:111-122.
10. Kim YH, Carraway ER. Dechlorination of pentachlorophenol by zero valent iron and modified zero-valent irons. Environ. Sci. Technol. 2000;34:2014-2017.
11. Hafez H. A study on the use of nano/micro structured goethite and hematite as adsorbents for the removal of Cr (III), Co (II), Cu (II), Ni (II), and Zn (II) metal ions from aqueous solutions. Int J Eng Sci. 2012;4:3018–3028.
12. Gupta A, Yunus M, Sankararamakrishnan N. Zerovalent iron encapsulated chitosan nanospheres - a novel adsorbent for the removal of total inorganic arsenic from aqueous systems. Chemosphere. 2012; 86(2):150-155.
13. Palma L, Gueye MTE, Petrucci E. Hexavalent chromium reduction in contaminated soil: A comparison between ferrous sulphate and nanoscale zero-valent iron. J. Hazard. Mater. 2015;281:70-76.
14. Mkpaoro MIF, Okpokwasili GC, Joel OF. A review of drill-cuttings treatment and disposal methods in Ngeria-The gaps and way forward. Proceedings of the Society of Petroleum Engineers, SPE-140720t, Annual International Conference and Exhibition, Lagos, Nigeria; 2015.
15. National Bureau of Statistics (NBS)' National Population Census (NPC), Federal Republic of Nigeria. 2006.
16. Ekubo A, Abowei J. Aspects of Aquatic Pollution in Nigeria. Research Journal of Environmental and Earth Sciences. 2011;3(6):673-693.
17. Adati AK. Oil exploration and spillage in Niger Delta of Nigeria. Civil. Environ. Res. 2012;2:2222-2863
18. Ziegler CK. Using mathematical models to assess sediment stability. Integrated Enviro-nmental Assessment and Management. 2005;2(1):44-50.
19. Nwaogazie IL. Probability and Statistics for Science and Engineering Practice (3rd ed.). Enugu, Nigeria: De- Adroit Innovation. 2011.
20. U.S. Environmental Protection Agency (US-EPA). Nanotechnology for Site Remediation Fact Sheet: EPA 542-08-009. (October 2008). Retrieved from www.epa.gov (accessed June 8, 2009). 2008.
21. Soegianto A, Irawan B, Affandi M. Toxicity of drilling waste and its impact on gill structure of post larvae of tiger prawn (Penaeus monodon). Global Journal of Environmental Research. 2008;2:36-41.
22. Zovko M, Romic M. Soil contamination by trace metals: Geochemical behavior as an element of risk assessment. In Dar, I.A.,

(Ed). Earth and Environmental Sciences, InTech. Rijeka. 2011;437-456.

23. Xie S, Jiang G, Chen M, Li Z, Huang X, Liang C. Harmless Treatment Technology of Waste Oil-Based Drilling Fluids. Petrol Sci Technol. 2014;32(9):1043-1049.
24. Shonkoff SBC, Hays J, Finkel ML. Environmental public health dimensions of shale and tight gas development. Environmental Health Perspectives. 2014;122(8):787–795.
25. Ludwig RD, Smyth DJA, Blowes DW, Spink LE, Wilkin RT, Jewett DG. Weisener CJ. Treatment of arsenic, heavy metals and acidity using a mixed ZVI-Compost PRB. Journal of Environmental Science and Technology. 2009;43:1970-1976.
26. Puls RW, Paul CJ, Powell RM. The application of in situ permeable reactive (zero-valent Iron) barrier technology for the remediation of chromate-contaminated groundwater: A field test. Journal of applied Geochemistry. 1999;14:989-1000.
27. Yang S, Lei M, Chen T, Li X, Liang Q, Ma C. Application of zerovalent iron (Fe0) to enhance degradation of HCHs and DDX in soil from a former organochlorine pesticides manufacturing plant. Chemosphere. 2010;79(7):727-732.
28. Tica D, Udovic M, Lestan D. Immobilization of potentially toxic metals using different soil amendments. Chemosphere. 2011; 85:577-583.
29. Karolina R, Katarzyna S, Paulina M, Jakub, M. Efficiency of Pb(II) and Mo(VI) removal by kaolinite impregnated with zero-valent iron particles. Mineralogia. 2017;48(1-4):71-86.
30. Kamunda C, Mathuthu M, Madhuku M. Assessment of radiological hazards from gold mine tailings in Gauteng province, South Africa. Int. J. Environ. Res. Public Health. 2016;13:138.
31. Clements K, Veil JA, Leuterman AJJ. Global practices and regulations for land application and disposal of drill cuttings and fluids. Proceedings of Society of Petroleum Engineers, SPE-126565, International Conference on Health, Safety and Environment in oil and Gas Exploration and Production, Rio de Janeiro, Brazil; 2010.
32. Henn K, Waddill DW. Utilization of nanoscale zero-valent iron for source remediation: A case study. Remediation. 2006;16:57-77.
33. Cundy AB, Hopkinson L, Whitby RLD. Use of iron-based technologies in contaminated land and groundwater remediation: A review. Elsevier; Science of the Total Environment. 2008;400:42-51.
34. Boparai HK, Joseph M, O'Carroll DM. Kinetics and thermodynamics of cadmium ion removal by adsorption onto nano zero-valent iron particles. J Hazard Mate. 2011;186:458–465.
35. Blowes DW, Puls RW, Bennett TA, Gillham, RW, Hanton-Fong CJ, Ptacek CJ. In-situ porous reactive wall for treatment of Cr VI and trichloroethylene in groundwater. Proceedings of 1997 International Containment Technology Conference and Exhibition,St. Petersburg, Florida. 1997a;851-857.
36. Esam HA, Mohamed H. Removal efficiency of the Heavy Metals Zn(II), Pb(II) and Cd(II) by Saprolegnia delica and Trichoderma viride at different pH values and Temperature Degrees. Mycobiology. 2007;35(3):135-144.
37. Munisha N, Dinesh S, Arun K. Removal of heavy metals from industrial effluent using bacteria. International Journal of Environmental Sciences. 2011;2:14-18.
38. Maddela NR, Reyes JJM, Viafara D, Gooty JM. Biosorption of Copper (II) by the microorganisms isolated from the crude-oil contaminated soil. Int. Journal of Soil and Sediment Contamination. 2015;24(8): 898-908.
39. Tayybah N, Muhammad DK, Iftikhar A, Shafiq R, Eui SR, Ijaz M, Muhammad J Biosorption of heavy metals by pseudomonas species isolated from sugar industry. Journal of Toxicology and Health. 2016;1-9.

Peer-review history:
The peer review history for this paper can be accessed here:
http://www.sciencedomain.org/review-history/27742