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Evaluation of the Efficiency of Local Clay in Mitigating Heavy Metal Pollution in Ballast Water: A Case Study of Calabar, Onne, and Warri Ports in the Niger Delta

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This study investigates the concentrations and removal efficiencies of heavy metals in ballast water from the ports of Calabar, Onne, and Warri, Nigeria, using local clay as a treatment method. The research focused on major ports within the Niger Delta region, where ballast and surface seawater samples were collected. Samples were obtained using cleaned plastic containers. Transportation and storage adhered to the D-2 standard to maintain sample integrity. Heavy metal analysis was conducted using flame atomic absorption spectroscopy (FAAS), with high-purity reagents and rigorous calibration procedures. Initial analysis revealed significant contamination with lead (Pb), zinc (Zn), copper (Cu), and cadmium (Cd), exceeding the limits set by the National Environmental Standards and Regulations Enforcement Agency (NESREA) and, in some cases, the International Maritime Organization (IMO). Lead concentrations were 0.279 mg/L in Calabar, 0.294 mg/L in Onne, and 0.235 mg/L in Warri, all surpassing the NESREA limit of 0.001 mg/L and the IMO limit of 0.250 mg/L. Zinc levels reached 0.83 mg/L in Calabar, 1.08 mg/L in Onne, and 2.75 mg/L in Warri, significantly exceeding both the NESREA limit of 0.02 mg/L and the IMO limit of 0.200 mg/L. Copper and cadmium concentrations also notably exceeded NESREA guidelines. Post-treatment analysis showed reductions in heavy metal concentrations, with varying effectiveness across different elements and ports. Lead levels in Calabar, Onne, and Warri were reduced to 0.172 mg/L, 0.278 mg/L, and 0.242 mg/L, respectively, with Calabar meeting the IMO limit. Zinc concentrations were lowered to 0.214 mg/L in Calabar, 0.911 mg/L in Onne, and 1.114 mg/L in Warri, with Calabar meeting the IMO limit but all samples still exceeding NESREA guidelines. Cadmium levels were significantly reduced to 0.002 mg/L in Calabar and Onne, and 0.005 mg/L in Warri, yet remained above NESREA limits. The percentage removal efficiencies for heavy metals after treatment with local clay revealed a 38.35% reduction in lead in Calabar, 5.44% in Onne, and an unexpected increase of 2.98% in Warri. Zinc removal was highest in Calabar at 74.22%, moderate in Warri at 59.49%, and lowest in Onne at 15.65%. Cadmium removal was highly effective in Calabar and Warri, with reductions of 88.89% and 92.96%, respectively, but was ineffective in Onne (0.00%).The use of local clay demonstrated significant potential in reducing heavy metal concentrations in ballast water, particularly for elements like zinc and cadmium. However, further optimization of the treatment process is needed to achieve consistent and comprehensive removal across different ports and heavy metals, ensuring compliance with stringent environmental standards.

Keywords: Heavy metals, ballast water treatment, local clay, Niger Delta ports, flame atomic absorption spectroscopy (FAAS), environmental standards, removal efficiency.

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INTRODUCTION

Maritime transportation is essential for global trade, but ballast water, used for maintaining ship stability, poses hidden environmental risks (Batra & Imran, 2022).. When released, ballast water can introduce invasive species and harmful chemicals into marine ecosystems, threatening biodiversity, local economies, and public health. The Niger Delta, a region with a unique environment and substantial economic significance for Nigeria (Abdulkadir & Mashood, 2021) is especially vulnerable to the ecological damage caused by ballast water discharges at its major ports, such as Warri, Onne, and Calabar.

To mitigate risks from Ballast water discharges, , international regulations like the Ballast Water Management Convention (BWMC) have been implemented, mandating ships to manage their ballast water to prevent the spread of invasive species and toxic chemicals(Bailey, 2015). However, compliance and enforcement in regions like the Niger Delta remain challenging due to limited resources and infrastructure. Strengthening local policies, enhancing port facilities, and increasing awareness among maritime operators are critical steps to protect the Niger Delta's fragile ecosystem (Čampara et al. 2019; Lin et al. (2021). Additionally, collaboration between governmental bodies, international organizations, and local communities is essential to develop sustainable solutions that balance economic growth and environmental protection (Hasanspahić et al. 2022; Osuji & Agbakwuru, 2022)

Purpose of the Research

The purpose of this research is to characterize and evaluate the quality of ballast water obtained from ships at Nigeria's major ports in the Niger Delta region, specifically Warri, Onne, and Calabar. This study investigates the concentrations and removal efficiencies of heavy metals in ballast water from the ports of Calabar, Onne, and Warri, Nigeria, using local clay as a treatment method. The research focused on major ports within the Niger Delta region, where ballast and surface seawater samples were collected. of the ballast waters, and design and implement a ballast water treatment process using locally sourced clay soil from Delta State as a filtration material. The NESREA Act sets forth stringent regulations to control marine pollution (Ladan, 2012).By achieving these objectives, the research seeks to understand the environmental impact of ballast water discharges and explore potential treatment methods to mitigate these effects, thereby protecting the region's unique ecosystem.

METHODOLOGY

The research areas include three major ports namely the Calabar, Warri and Onne sea ports strategically located within the Niger Delta region of Nigeria.Sampling Methods

Ballast as well as surface seawater sampling was conducted in the main ports of the Niger Delta, including Warri, Onne, and Calabar Ports. These ports are the primary and most extensive ports in Nigeria. The samples were collected in plastic containers that were washed with non-ionic detergent. They were then rinsed with tap water, and again with de-ionized water before being used. Grab samples were collected at the ports, combined to create a composite sample, and routinely stored in a refrigerator at about 4^{o}C before analysis. Samples were designated (BWC, SWC, BWO, SWO, BWW, SWW). Where BWC=Ballast Water Calabar, BWO=Ballast Water Onne, BWW= Ballast Water Warri, SWC=Surface Water Calabar, SWO=Surface Water Onne, SWW= Surface Water Warri.

Transportation of Samples and Pre-treatment

Following Guidelines G8, samples were analyzed promptly after sampling, within 6 hours, and preserved appropriately to maintain the integrity of the organisms and enable accurate analysis (Gollasch & Kacan, 2015). The collected samples were delivered to the laboratory in accordance with the D-2 standard. Watertight sample vials were utilized to prevent water seepage during transportation. The samples were transported in Styrofoam cartons to prevent abrupt temperature fluctuations (Gollasch & David, 2011). The samples were stored at a temperature differential of 10–15 °C between the ambient sampling conditions and during storage. This was done to prevent possible temperature shock and stress generated by warm atmospheric condition (Gollasch & Kacan, 2014).

High-purity analytical grade reagents were used, including HNO_3 (69% LR, Breckland Scientific Supplies, U.K), for sample preservation before analysis. Only distilled water was utilized in the experiment to create the solutions. For the metal analysis process, atomic absorption spectroscopic standard solutions with a concentration of 1000 mg L^{-1} (Buck Scientific) were utilized to create intermediate and working standards.

The intermediate standards were created using the dilution procedure. The working standard solutions were freshly created by diluting the intermediate standards with distilled water. The heavy metals (Hg, Fe, As, Zn, Cu, Cd, and Ni) were examined using a flame atomic absorption spectrometer (FAAS) with calibration curves. Prior to analysis, the instrument parameters (lamp alignment, wavelength and slit width adjustment, and burner alignment) were fine-tuned to enhance signal intensity and sensitivity. The quantification of heavy metals was performed using the Agilent 55AA Flame Atomic Absorption Spectrometer (FAAS).

Ballast Water Treatment System

The materials consist of untreated clay (NT) collected from Udu area in Aghalokpe town, Delta State, Nigeria, which was treated with hydrochloric acid (HCl) and labelled as (AT). A solution was prepared by dissolving 50 g of NT in 100 millilitres of 4N HCl solution. The mixture was agitated for 1 hour and then left undisturbed for 24 hours. Finally, it was decanted and rinsed extensively with distilled water. The filtrate was dehydrated in an oven at 140 °C for 4 hours. The material was cooled, ground, and sifted into particles measuring around 125 micrometres before being stored securely for future use.The Thermo Electron Nicolet 4700 FTIR spectrometer captured the spectra of the adsorbent with a resolution ranging from 4000 to 500 $cm^{-1.}$

The characteristics of the clay soil were analyzed using Thermo Scientific X-ray Fluorescence (XRF) spectroscopy. XRF analysis was conducted using the usual procedure using Montana soil SRM 2710 for Geological Sample and IAEA – 155. Weighed two grams of each sample and placed them in a sample holder, covering them with cotton wool to prevent splashing. The sample holders with the sample were evacuated using a vacuum pump for 10 minutes before being placed into the XRF Spectrometer for Elemental analysis. The procedure was calibrated using geological standards, and the analysis can be conducted in either elemental or oxide form. The samples were analyzed in the XRF spectrometer for 10 minutes each, and the findings were obtained (Ogundiran & Kumar, 2015).X-ray Diffraction (XRD) analyses were conducted using a PW2400 and MD 10 Randicon diffractometer, respectively.

RESULTS

The results from an X-ray diffraction (XRD) analysis of the clay soil us for the filtration process, specifically focused on determining the soil crystallite size, The crystallite sizes of the clay particles, calculated for the different peaks, range from approximately 23.46 nm to 56.89 nm. The overall average particle size calculated is approximately 46.62 nm. This indicates that the clay sample consists of nanosized crystallites, which can affect its physical and chemical properties.

Table 1: Concentrations of Heavy Metals in Ballast Water before Treatment in studied Ports (mg/L)

Element/ Samples	Pb (mg/L)	Hg (mg/L)	Fe (mg/L)	As (mg/L)	Zn (mg/L)	Cu (mg/L)	Cd (mg/L)	Ni (mg/L)
BWC	0.279±0.120	ND	0.66±0.30	ND	0.83±0.22	1.06±0.035	0.018±0.00	0.83±0.22
BWO	0.294±0.006	ND	0.96±0.00	ND	1.08±0.00	1.18±0.00	0.002±0.00	0.65±0.820
BWW	0.235±0.036	ND	1.95±0.58	ND	2.75±0.141	2.26±0.92	0.071±0.005	2.67±0.07
IMO Guidelines	≤0.250	≤0.0007	-	≤0.050	≤0.200	≤5.00	≤3.00	≤50
NESREA	≤1 μg/L	≤0.05 μg/L	-	≤20 μg/L	≤20 μg/L	≤5 μg/L	≤1 μg/L	-

ND = Not Detectable; BWC=Ballast Water Calabar, BWW= Ballast Water Warri, BWO= Ballast Water Onne; IMO = International Maritime Organization; NESREA (National Environmental Stand

Table 1 presents the concentrations of various heavy metals in ballast water samples collected from three ports: Calabar (BWC), Onne (BWO), and Warri (BWW). The analysis of ballast water from the ports of Calabar, Onne, and Warri reveals significant heavy metal concentrations that exceed the established guidelines. Specifically, lead concentrations are 0.279 mg/L in Calabar, 0.294 mg/L in Onne, and 0.235 mg/L in Warri, all of which surpass the NESREA limit of 0.001 mg/L and the IMO limit of 0.250 mg/L. Zinc levels are also high, with 0.83 mg/L in Calabar, 1.08 mg/L in Onne, and 2.75 mg/L in Warri, exceeding both the NESREA limit of 0.02 mg/L and the IMO limit of 0.200 mg/L. Copper concentrations are 1.06 mg/L in Calabar, 1.18 mg/L in Onne, and 2.26 mg/L in Warri, far exceeding the NESREA limit of 0.005 mg/L, though within the IMO limit of 5.00 mg/L. Cadmium levels, at 0.018 mg/L in Calabar, 0.002 mg/L in Onne, and 0.071 mg/L in Warri, also surpass the NESREA limit of 0.001 mg/L but are well within the IMO limit of 3.00 mg/L. Mercury and arsenic were not detectable in any samples, indicating compliance with the guidelines from both

IMO and NESREA. The iron concentrations are 0.66 mg/L in Calabar, 0.96 mg/L in Onne, and 1.95 mg/L in Warri, and nickel concentrations are 0.83 mg/L in Calabar, 0.65 mg/L in Onne, and 2.67 mg/L in Warri. These values are within the IMO limits, and there are no specified limits for iron and nickel from NESREA. Overall, the findings suggest a substantial presence of heavy metals in the ballast water, necessitating further treatment and mitigation measures to comply with the stricter NESREA guidelines and to reduce potential environmental hazards (Salleh et al. (2021).

Table 2: Mean Concentrations of Heavy Metals in Ballast Water after Treatment with Clay (n=3)

Element/ Samples	Pb (mg/L)	Hg (mg/L)	Fe (mg/L)	As (mg/L)	Zn (mg/L)	Cu (mg/L)	Cd (mg/L)	Ni (mg/L)
BWC	0.172±0.01	0.0001±0.00	0.449±0.01	ND	0.214±0.001	1.009±0.01	0.002±0.001	0.664±0.01
BWO	0.278±0.01	0.0001±0.00	0.489±0.01	ND	0.911±0.001	1.009±0.01	0.002±0.001	0.013±0.01
BWW	0.242±0.01	0.0001±0.00	1.204±0.01	ND	1.114±0.01	2.706±0.01	0.005±0.001	0.423±0.01
IMO Guidelines	≤0.250	≤0.0007	-	≤0.050	≤0.200	≤5.00	≤3.00	≤50
NESREA	≤1 µg/L	≤0.05 µg/L	-	≤20 µg/L	≤20 µg/L	≤5 µg/L	≤1 µg/L	-

ND = Not Detectable; BWC=Ballast Water Calabar, BWW= Ballast Water Warri, BWO= Ballast Water Onne; IMO = International Maritime Organization; NESREA (National Environmental Standards and Regulations Enforcement Agency)

Table 2 presents results of the analysis of ballast water from the ports of Calabar, Onne, and Warri after treatment with clay reveals notable changes in heavy metal concentrations. Lead concentrations are 0.172 mg/L in Calabar, 0.278 mg/L in Onne, and 0.242 mg/L in Warri. While the Calabar sample now meets the IMO limit of 0.250 mg/L, the Onne and Warri samples still exceed this limit. All samples remain above the NESREA limit of 0.001 mg/L. Mercury concentrations are 0.0001 mg/L in all samples, which are well below both the IMO limit of 0.0007 mg/L and the NESREA limit of 0.00005 mg/L.

Iron concentrations are 0.449 mg/L in Calabar, 0.489 mg/L in Onne, and 1.204 mg/L in Warri. There are no specific guidelines from IMO or NESREA for iron concentrations in ballast water. Arsenic was not detectable in any of the samples, indicating compliance with both IMO and NESREA guidelines.Zinc levels are 0.214 mg/L in Calabar, 0.911 mg/L in Onne, and 1.114 mg/L in Warri. The Calabar sample meets the IMO limit of 0.200 mg/L but exceeds the NESREA limit of 0.02 mg/L. Both Onne and Warri samples exceed both the IMO and NESREA limits. Copper concentrations are 1.009 mg/L in Calabar and Onne, and 2.706 mg/L in Warri, all within the IMO limit of 5.00 mg/L but exceeding the NESREA limit of 0.005 mg/L.

Cadmium levels are 0.002 mg/L in Calabar and Onne, and 0.005 mg/L in Warri, which, while within the IMO limit of 3.00 mg/L, exceed the NESREA limit of 0.001 mg/L. Nickel concentrations are 0.664 mg/L in Calabar, 0.013 mg/L in Onne, and 0.423 mg/L in Warri, all within the IMO limit of 50 mg/L. NESREA does not specify a limit for nickel. The results indicate that the clay treatment has reduced the concentrations of some heavy metals, bringing some within the IMO guidelines (IMO, 2004; Jang, et al., 2020).), but further reductions are necessary to meet the stricter NESREA guidelines and mitigate potential environmental hazards.

Table 3: Percentage Removal of Heavy Metals from Ballast Water after Treatment with Local Clay

Element	Location of port/ percentage reduction in heavy metal conc.		
	BWC (%)	BWO (%)	BWW (%)
Pb	38.35	5.44	-2.98
Hg	0.00	0.00	0.00
Fe	31.97	49.06	38.26
As	0.00	0.00	0.00
Zn	74.22	15.65	59.49
Cu	4.81	14.49	-19.73
Cd	88.89	0.00	92.96
Ni	20.00	98.00	84.16

BWC= Ballast Water Calabar BWO = Ballast Water Onne, BWW = Ballast Water Warri, The analysis of the percentage removal of heavy metals from ballast water after treatment with local clay reveals varying degrees of effectiveness across different ports and elements. For lead (Pb), there was a 38.35% reduction in Calabar, a minimal 5.44% reduction in Onne, and an unexpected increase of 2.98% in Warri. Mercury (Hg) showed no reduction in any of the ports, with 0.00% removal across Calabar, Onne, and Warri. Iron (Fe) reductions were 31.97% in Calabar, 49.06% in Onne, and 38.26% in Warri, indicating significant but variable effectiveness. Arsenic (As) removal was also 0.00% in all ports, indicating no detectable change. Zinc (Zn) reductions were substantial in Calabar at 74.22%, moderate in Onne at 15.65%, and significant in Warri at 59.49%. For copper (Cu), there was a minor reduction of 4.81% in Calabar, 14.49% in Onne, and a notable increase of 19.73% in Warri, indicating inefficacy or possible contamination in the latter.

Cadmium (Cd) removal was highly effective in Calabar and Warri, with reductions of 88.89% and 92.96%, respectively, while Onne showed no reduction at 0.00%. Nickel (Ni) reductions were 20.00% in Calabar, a highly effective 98.00% in Onne, and 84.16% in Warri. The treatment with local clay demonstrated variable effectiveness, with notable reductions in some metals such as zinc and cadmium, while showing limited or no effectiveness in others such as mercury and arsenic. Further optimization of the treatment process may be necessary to achieve more consistent and comprehensive removal of heavy metals across different ports and elements.

CONCLUSION

Ballast waters in the Niger Delta do not fully comply with IMO D1 regulations. Untreated discharges pose risks of eutrophication, biodiversity alteration, pollutant bioaccumulation, and the spread of invasive species and pathogens (IMO, 2004; Osuji& Agbakwuru, 2022). According to the NESREA Act (Ladan, 2012), compliance with marine pollution standards is critical for environmental protection in Nigeria.Implementing stricter ballast water discharge regulations and exploring affordable treatment alternatives, like using local clay, are crucial for protecting Nigeria's marine ecosystem.Nigeria cannot afford to neglect its marine environment. Pollution of the marine environment with heavy metals will be detrimental to both the health and economic development of Nigeria (Pona et al. (2021). The study recommends implementing more stringent restrictions on ballast water discharges to safeguard Nigeria's marine ecosystem. Exploring affordable ballast water treatment alternatives, such as using local clay, is essential. Additionally, further studies are required to establish the efficacy of local clay soil for treating ballast water before it is discharged into the environment. This approach aims to ensure that ballast water discharges do not lead to eutrophication, biodiversity alteration, pollutant bio-accumulation, or the spread of invasive species and pathogenic microbes in the Niger Delta.

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Appendix

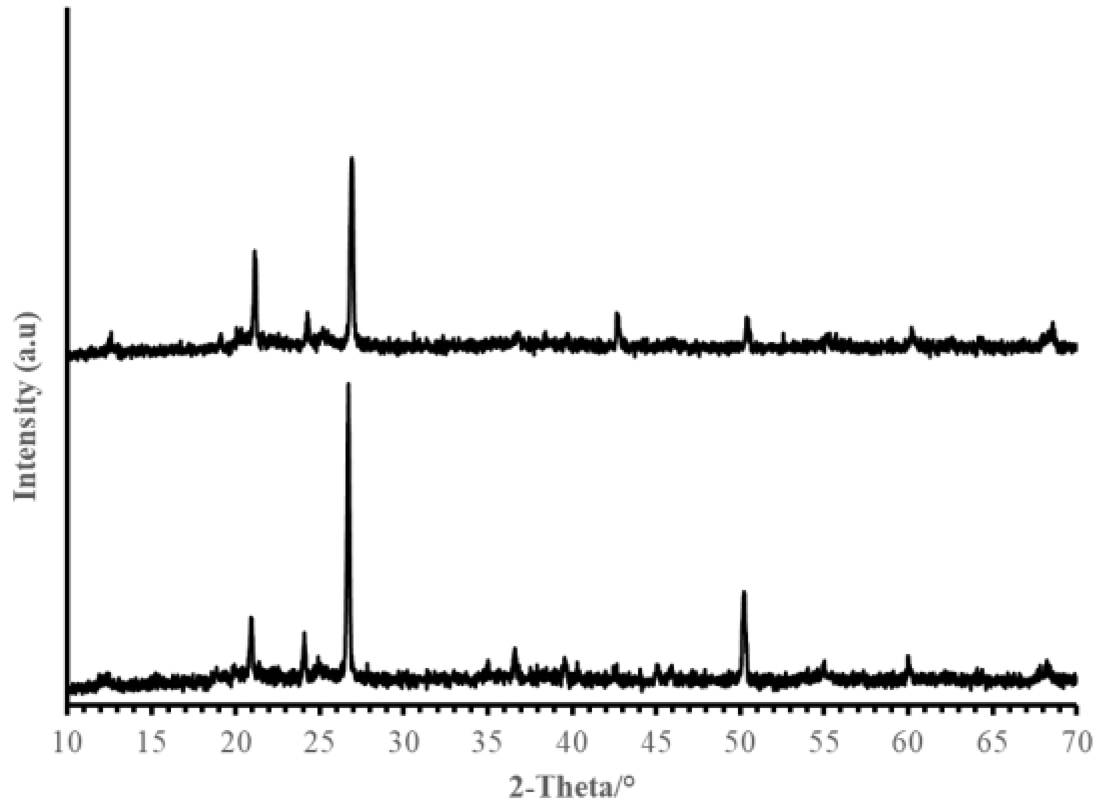

Figure 1. X-ray diffraction patterns of Natural Clay

Different peaks observed in the Clay XRD pattern

2-Theta °	FWHM	Theta	COS-Theta	FWHMrad	Size
19.14	0.14	9.57	0.986083222	0.002443784	55.92602888
21.16	0.14	10.58	0.9829995	0.002443784	55.75113462
24.29	0.16	12.145	0.977618301	0.002792896	48.51519589
26.91	0.17	13.455	0.972552968	0.002967452	45.42477566
36.86	0.16	18.43	0.948710608	0.002792896	47.08062538
42.66	0.13	21.33	0.931500902	0.002269228	56.89424995
50.41	0.18	25.205	0.904789893	0.003142008	39.91201778
55.12	0.30	27.56	0.886526805	0.00523668	23.46383877
					46.62098337

size = Kλ/βcosθ

K=0.9

β = FWHM

λ = 1.54 Å = 0.154 nm

Particle size = 46.62 nm