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Full Length Research Article

INVESTIGATION OF THE EFFECTIVENESS OF FENTON OXIDATION FOR REMEDIATING BALLAST WATER CONTAMINATED SOIL

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ABSTRACT
Ballast water released from ships have been known to contaminate water bodies and soils and introduce invasive species into the immediate environment, if not properly treated or if not treated at all. There is therefore a need to design several strategies in preventing and/or ameliorating this and to establish the effectiveness of each strategy. This paper therefore investigates the effectiveness of the use of fenton oxidation in the remediation of ballast water contaminated soil. Soil samples were collected from Otorho Abraka and stimulated with ballast water in a laboratory scale experiment. The soil samples were mixed with solutions containing hydrogen peroxide and ferrous ions at varying concentrations. The reaction proceeded for twelve (12) weeks, then the samples were analyzed for removal of contaminants. There was pH reduction from 5.10 to 4.00, but increase in the total organic carbon from 2.80% to 3.40%. Total phosphorus was between 7.20 - 453mg/l, while total nitrogen ranged from 1.70mg/l to 2.10mg/l. There was also an increase in heavy metal content. Soil texture was slightly affected with Fenton reagent. The result showed a significant reduction in the concentration of pollutants with time, since more hydroxyl radicals reacted with the contaminants. Its efficiency and kinetics was established as first-order reaction.

Keywords: Ballast water, pH, Oxidation, Remediation, Concentration.

INTRODUCTION
Seawater taken on hold in a ship while on board to maintain stability while moving from one shoreline to another within the same or different country and discharged before loading or unloading is called ballast water (Chen *et al*., 2022). Fresh or seawater held in the ballast tank and cargo hold of ship are used to provide stability during loading and unloading activities; and it has been previously established that the ballast water of maritime vessels pose a major threat to the environment due to the transportation of invasive marine species into new environments (Sayinli *et al*., 2022). It contains organisms that are exclusive and indigenous to the specific region where the ballast water is taken to fill the vessel's tank (Ware *et al*., 2016). This translocation of species can cause changes in the biodiversity of oceans and coastal waters. The International Maritime Organization (IMO) estimated that over 7,000 species are transferred in ballast water tanks of maritime vessels every day. There is also movement of organic and inorganic matter, heavy metals and sediment present in the ballast water, which is also a critical factor in spreading pollution and demanding ecological balance (GEF-UNDP-IMO, 2010).

Geological, climatic, seasonal and environmental conditions have influence on seawater quality, which is determined by the turbidity, salinity, temperature, dissolved Oxygen (DO) content, polycyclic aromatic hydrocarbon (PAHs), heavy metals and marine species. In order to prevent pollution from the translocation of ballast water, it should be treated and disinfected in accordance with prevailing legislation. The risk parameters can be classified as physical, economic, capital, environmental (emphasizing residual toxicity and safety), and biological meaning the organism treated and the inactivation efficacy (Chen *et al.*, 2022). These treatments are based on the location, biota and indigenous, morphology and evolution stages of organisms can affect the inactivation efficiency of the ballast treatment method (Vijayan *et al*., 2020).

The pH level and electrical conductivity of ballast water can indicate its level of toxicity. The chemical assessment of water bodies is an indication of the health safety of the water ways and the purpose for which it is used for. The D1 mechanism involves mechanical, physical or chemical, treatments involving ship exchange of ballast water in open sea or coastal area. Fenton oxidation method is an advanced remediation technique for treating contaminated soil. It involves using hydrogen peroxide and ferrous ion to create a highly reactive hydroxyl radical (OH^-) capable of breaking down organic contaminants to harmless byproducts. Its effectiveness was evaluated for remediation of soil contaminated with ballast water.
The D2-standard specifying the maximum amount of viable organism allowed to be discharged, including specified indicator microbes harmful to human health. A most effective way to protect the quality of water either surface or ground water bodies is to develop a monitoring scheme to assist in the planning, development and guiding human activities to minimize adverse impact on water quality. Using the D1 and D2 methods. D1 involves mechanical, physical or chemical involves ship exchange of ballast water in an open sea away from coastal areas and D2 standard specifying the maximum amount of viable organism allowed to be discharged, including specified indicator microbes harmful to human health (Sayinli *et al*., 2022). Studies have confirmed that heavy metals can directly influence behaviour by impairing mental, neurological function and alters metabolic processes. The control of ballast water has become an international issue by International Marine Organization (IMO). There has been global temperature increase by 0.2°C in the last decade, which has effect on man, plants and microorganisms. World Health Organization guideline for re-use of effluents revised in 2011 along with several other legislations and guidelines have been developed (Grob and Pollet, 2016).

The IMO regulation established the D-2 standard for ballast treatment which stimulate water quality standard and ballast water discharge after treatment using approved ballast water treatment system (BWTS) (Alba *et al.,* 2021). Physical and mechanical treatment technologies include filtration, cyclone separation, heating and ultra-sonic treatment. Chemical treatment using chlorine gas may corrode tanks and ballast water tank (Sayinli *et al.*, 2022). In addition, toxic chemicals and volatile disinfection by-products generated during the treatment processes pose a danger to crew members, human health and the environment (Wang and Corbett, 2020; Xiao *et al.*, 2023). Studies have estimated that the global economic cost of invasive species caused by ballast water discharge was approximately, $162-167 billion (Wright, 2019; Wang *et al*., 2020).

Ballast water in Nigeria is still indiscriminately discharged without regard to the environmental safety. The purpose of this study was to determine the effect of ballast water on the physic-chemical properties of soil, test the potential of Fenton reagent on contaminated soil, the kinetics of chemical oxidation process and contribute to available information on environment clean up regarding ballast water discharge.

MATERIALS AND METHODS

Study Area

Nigeria Port Authority (NPA) is located in Warri, Delta State. It is located between latitudes $5^0$51'N and $5^0$55'N and longitude $5^0$46'E and $5^0$75'E. The area is swampy, low-lying and mostly water-logged. It lies in the rainforest and mangrove belt of Nigeria. It is a subequatorial climate and the soil nutrient deficient and sandy. The climate is humid with thick forest vegetation of the Niger River. Warri has a seaport, an airport and some oil and gas companies. People in the area engage in trading, fishing, tapping of palm wine, lumbering among others activities.

Collection of Samples and Processing

Ballast water samples were collected from vessel labelled VARDAR, having a tag of 53812 CBN and carrying multiple dry cargo with 175 m length and 30 m beam (width). It has a weight of 1,800 N, was from South Africa, and birthed in Nigeria Port Authority (NPA), Warri. Soil samples used for this study were collected from a rural area in Otorho Abraka community in Ethiope East Local Government Area of Delta State. It was collected with soil Auger into a polythene bag and taken to the laboratory. Debris, wood and stones in the soil were removed and air-dried for 2 weeks in the laboratory. It was filtered into a plastic container and sieved with 850 micrometer sized mesh. Hydrogen peroxide and iron sulphate fenton reagents were purchased from Sonitex Supply Pyrex Company in Edo State, Nigeria.

About 20g of air-dried soil sample was passed through 2mm sieved into 50 mL beaker, then 20mL of distilled water was added and allowed to stand for 30mins with occasional stirring by means of a glass rod. The filtrate from suspension was used for analysis. The pH was determined using HACH pH meter (HQ20), while electrical conductivity was measured using HACH CENSION 5 model. Total phosphorus, total organic carbon, total nitrogen, total petroleum hydrocarbon were all measured using HACH DR 2010 spectrometer, following the method described by APHA (2012). Heavy metal analysis was done using AAS according to APHA, (2010). Particle size was determined using the method described by Sayinli (2022).

Remediation of Ballast Water Contaminated Soil

About 2kg of the sieved soil sample was poured into a plastic container and polluted with 200 mL of ballast water to achieve 20% pollution level. It was properly mixed and kept for analysis. About 50% volume of $FeSO_4$ and 50% H_2O_2 by volume each were introduced into 2 kg of the polluted soil in 1:5 ratio (i.e. 5% of $FeSO_4$ treatment solution equivalent to 50 mL $FeSO_4$ and 250 mL H_2O_2 per kg of stimulated soil). It was thoroughly stirred to mix to ensure thorough oxidation. Aliquot of soil samples were collected for analysis and remediation monitored for 12 weeks (Caroline and Bruno, 2016; Ignacio *et al.*, 2021). Total petroleum hydrocarbon, physico-chemical, particle size, as well as heavy metals of the soil were determined prior to and after simulation to ascertain the extent and effect of ballast water pollution on the soil parameters. The pH and TPH were monitored weekly for 12 (twelve) weeks, during which the parameters were measured.

RESULTS AND DISCUSSION

The results of the physico-chemical properties of the soil before contamination, the contaminated soil and the treated soil are shown in Table 1.

Table 1: Physico-chemical parameters of soil sample and effect of remediation.

Parameter	Soil	Soil + Ballast Water	After remediation
pH	5.1	4.0	3.7
Electrical conducting (µS cm^{-1})	193.9	1234.1	1102.1
Total Phosphorus (mg kg^{-1})	7.2	452.1	5.2
Total Nitrogen (mg l^{-1})	1.7	2.1	1.5
Chloride (mg l^{-1})	102	831.2	93
Total Organic Carbon (%)	2.8	3.4	2.3
Total Petroleum Hydrocarbon (mg l^{-1})	10.3	1283	221.1
Cadmium (mg l^{-1})	0.12	0.23	0.00
Iron (mg l^{-1})	0.6	1.50	0.30
Lead (mg l^{-1})	ND	ND	ND
Copper (mg l^{-1})	0.01	0.03	ND
Zinc (mg l^{-1})	0.21	1.13	0.4
Particle size distribution (%)			
Sand	53.1	56.3	52.40
Clay	9.3	8.4	6.00
Silt	3.0	2.7	2.90

The decrease in pH is graphically presented in Figure 1

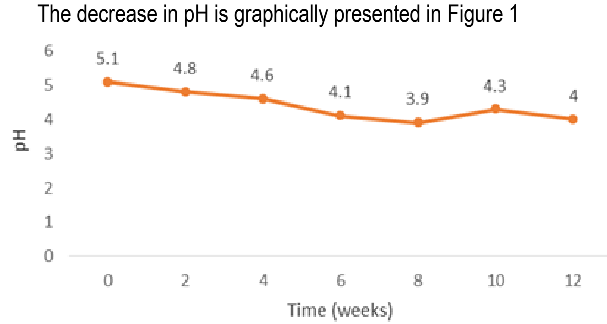

Figure 1: Change in pH with time of remediation process

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Figure 2 depicts the percentage decrease of total petroleum hydrocarbon (TPH) with time during the remediation process. The longer the time of contact, the greater the decrease in total petroleum hydrocarbon.

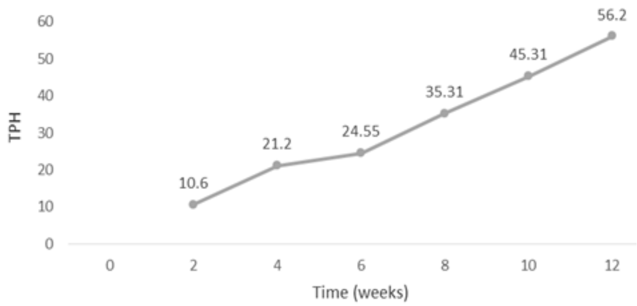

Figure 2: Percentage decrease of total petroleum hydrocarbon in remediation process.

Figure 3 shows the change in total petroleum hydrocarbons over the treatment period.

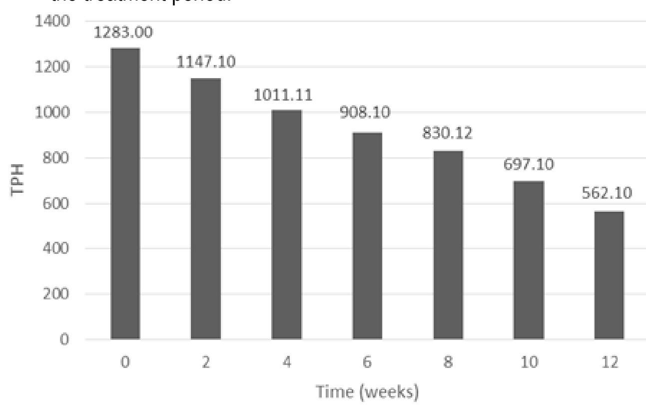

Figure 3: Change in Total Petroleum Hydrocarbon (TPH) with time during remediation process

The kinetic data for the remediation by Fenton oxidation is presented in Figure 4.

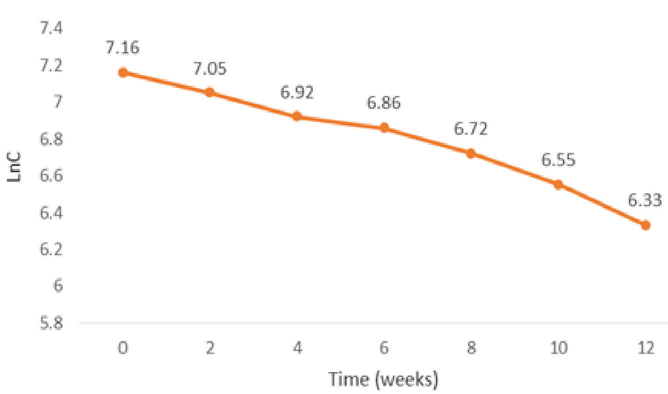

Figure 4: Remediation by Fenton oxidation kinetic data

From the results in Table 1, the pH values decreased from 5.1 to 4.0 after its contamination with ballast water, which is below the standards recommended by WHO (Apetroaei *et al.*, 2018) and NESREA (Tsolaki and Diamadopoulos, 2009). The concentration of phosphorus showed that after contamination with ballast water, it was higher than WHO limits (Unal, 2023). Apetroaei *et al.*, 2018 stated that high concentration of phosphate of this value is an indication that ballast water is polluted and can result in eutrophication. This could be due to dissolved substances (nutrients) such as nitrates and phosphate. Total organic carbon was increased which could be due to the carbonaceous nature of ballast water, so also was nitrogen which is a nutrient. Electrical conductivity increased from 193.9 to 1243.1 µS cm^{-1} which may affect the ionic properties of soil, i.e. non-polar hydrocarbons have immobilized ions in the soil thus reducing ionic mobility. No significant change in particle size distribution was observed, but there was an increase in total petroleum hydrocarbon from 10.3 to 1283 mg kg^{-1} after contamination. There was an increase in Fe^{2+} and Zn^{2+}, which could be due to the material used in building the vessel, indicating the presence of heavy metals. Total organic carbon and total nitrogen increased after treatment of the soil with ballast water.

After the remediation process, electrical conductivity was observed to have decreased from 1243.1 to 1102.1 µS cm^{-1}. Heavy metal contents were also removed, showing the effectiveness of fenton oxidation process. Decrease in pH from 4.0 to 3.7 showed acidity of the soil. In the Fenton oxidation, it is influenced by contact time - the greater the contact time, the greater the decrease in the waste content (David and Gollasch, 2012). This decrease continued from 0-12 weeks. This is because the longer the contact time, the fenton process will produce more OH^- radicals, (Albert *et al.*, 2016) so that it can oxidize organic matter into smaller elements and improve processing efficiency. Hydrogen peroxide and iron sulphate have been shown to reduce the pollution parameters in ballast water, when added to the soil with time (Gracki *et al.*, 2002). Figure 4 shows a plot of LnC against time (weeks) with a slope = ΔLnC/Δtime; which was finally resolved as slope = y = mx+c.

Conclusion

From the findings, it could be concluded that ballast water contamination affects the physico-chemical properties of the soil imparted with it by decreasing pH, TPH, heavy metals, electrical conductivity, total nitrogen and total phosphorus contents. The trend showed that remediation by fenton oxidation method could restore almost the originality of the affected soil with time and it is a first-order kinetic reaction

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