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EFFECT OF pH ON THE REMOVAL OF METAL IONS ASSOCIATED WITH PRODUCED WATER ON PULVERIZED OYSTER SHELLS (OS) AS ADSORBENT

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ABSTRACT

This research aims to investigate the effect of variation of medium pH on Metal ion sorption potentials of pulverized Oyster Shells as adsorbent in produced water from selected flow stations in the Niger Delta region of Nigeria. Produced water samples were collected from six (6) different oil drilling installations (CC7T, CC8T, WELL 2 GSS, WELL 8 TEB, AZUZUAMA ST 1, AZUZUAMA ST 2) around the Niger Delta area of Nigeria. Atomic Absorption Spectrometer (AAS) was used to determine selected metals; Nickel (Ni), Cobalt (Co), Copper (Cu), Iron (Fe), Lead (Pb), Calcium (Ca) and Potassium (K) concentrations before and after adjustment of pH of the medium. The results obtained showed that Nickel, Iron and Lead were completely removed from the produced water at a pH of 11.1 while Cobalt, Copper, Calcium and Potassium concentrations were not affected by adjusting the pH either in the acidic or basic ranges. There were small and slight reductions of Nickel, Iron and Lead in the acidic pH of 5.6. The study underscores the need to further compare the above method's efficiency with other detoxification technologies like Detoxification by chemical reaction (DCR) technology which appears to be more effective, efficient and environmentally friendly.

Keywords: Pulverized Oyster Shell, pH, Sorption, DCR Technology, Produced Water

INTRODUCTION

Globally, oilfield produced water (OPW) production is expected to increase due to increased demand for crude oil, coupled with increased global production activity. The current forecast shows a two-fold increase in produced water volume globally over the next 10 years from about 158,900 million barrels per day (mb/d) to 243,000 million barrels per day (mb/d). Produced Water Society (2020). With the rapid development of industrialization and urbanization, the content of heavy metals in the environment, urban and rural rivers and lakes significantly exceeds the standards. Especially, the toxic heavy metal ions have serious impacts on human health and the environmental ecosystem due to their physicochemical properties of non-degradable, highly virulent and widely dispersed in water solutions. There have been many reports on solid waste recycling as a resource to treat wastewater Mosley et.al. (2019), which are beneficial to improving the quality of the water environment by adsorbing heavy metal ions in water.

Oysters are common economic aquaculture organisms in coastal areas, and oyster shells (OS) are solid waste from production and processing. More than 60% of oyster shells (OS) are discarded on the beach and ultimately pollute the soil. OS can be made suitably into permeable oyster shell bricks (POSB) to adsorb heavy metal ions in water because of its high yield and special mesoporous structure.

Produced water is used in the oil and gas sector to describe the water that is associated with oil and gas during extraction. It is a mixture of formation water (water contained in the reservoir formation) and connate water (water injected into the reservoir to maximize hydrocarbon production and maintain reservoir pressure).Produced water is a byproduct of the oil and gas industry, containing a variety of contaminants, including heavy metals such as lead, cadmium, and mercury, which are known to be harmful to the environment and human health. The disposal of produced water has raised significant environmental concerns, as traditional treatment methods are often costly and inefficient. Nkanga et. al. (2024)

Oyster shells, composed primarily of calcium carbonate, have gained attention as a potential low-cost and sustainable material for the removal of heavy metals from wastewater. Oyster shells are abundant and readily available as waste products from the seafood industry, making them an attractive option for environmental remediation. Several studies have explored the potential of oyster shells as an adsorbent for metal removal, highlighting their high surface area, alkaline nature, and the presence of functional groups that can bind with metal ions. This research builds upon the existing literature to investigate the efficacy of oyster shells in removing specific metals from produced water. Nkanga et. al. (2024)

Oyster shells have been found to be effective in adsorbing heavy metal ions from water due to their high yield and special properties. Some of the metals that oyster shells can absorb include arsenic, cadmium, copper, and zinc. The absorption ability of oyster shells tends to increase with the initial concentration of the metal ions in the water. The efficiency of metal ion removal can vary depending on factors such as the particle size of the oyster shells and the pH of the water. Oyster shells can also adsorb metals beyond ion-exchange with calcium, as demonstrated by the secondary precipitation of metal carbonates on the shell surfaces. Additionally, the absorption of heavy metal ions can lead to a decrease in the surface area and pore volume of the oyster shells, Chen et. al. (2018).

Shell powders, derived from sources like oyster shells, and egg shells, which is essentially 90% ground $CaCO_3$have irregular Rhombohedral structure andpossess unique characteristics that make them effective adsorbents for heavy metal ions. These characteristics include high surface area, broader size distribution, porous structures, and the presence of functional groups, such as hydroxyl and carboxyl groups, which play a crucial role in metal ion binding.

Zhang et.al. (2019), Chikwe and Iwuoha (2024), Nkanga et.al. (2024). My research team in 2021used Oyster and snail shells differently to remediate heavy metal and crude oil contaminated soils in the Niger Delta and the results are promising from the data obtained from Oyster shells Onojake et. al. (2021).

The aim of this research is geared to investigating the absorbent/adsorbent potentials of pulverised Oyster shells for metal ions in produced water obtained at different crude oil wells in the Niger Delta, at varying pH values especially in acidic and alkaline ranges. The outcome will be informative enough to policy makers and Environmentalists interested in the conversion of abundant environmental waste material in the Niger Delta into huge and cost effective resource feedstock for detoxifying and decontaminating produced water with respect to toxic metals that is released in abundance to the environment as a result of crude oil exploration.

MATERIALS AND METHODS

Sample Collection

Produced water samples were collected from six (6) different oil drilling installations (CC7T, CC8T, WELL 2 GSS, WELL 8 TEB, AZUZUAMA ST 1, AZUZUAMA ST 2) around the Niger Delta area of Nigeria. The samples were collected and stored in a clean glass container, which was furthermore put into a cooler to regulate the temperature, as it was transported for analysis in an analytical laboratory. The waste oyster shell was collected in Akpan-Andem Market in Uyo, Akwa-Ibom State, Nigeria and washed in distilled water to remove residual sediments and musculature, and then dried in air.

METHOD OF ANALYSIS

Pre-Analysis Preparation and Sample Analysis Procedure

The produced water was separated using a separating to remove all crude oil in the sample before analysis. Oyster shells were air dried and ground to powdery form using the crusher. The oyster shell powder was then sieved to a mesh size of 1.18 mm. The sieved oyster shell powder (OSP) was then stored in a plastic container for further use. A separating funnel was mounted on a retort stand and 200ml of the produced water was poured into the separating funnel. 20mls of hexane (an organic solvent) was poured in the separating funnel and the funnel was corked and shook vigorously while intermittently opening the lower end of the funnel to allow the removal of air bubbles. The produced water mixture was shaken and hexane was returned to the retort stand allowing it to settle for two (2) minutes, after which water was removed from the separating funnel leaving behind the hexane. A column was created using layers of glass wool, sodium sulphate anhydrous and silica gel and the separated mixture was then passed through the column into a clean glass beaker.

Analysis of Heavy Metals in Produced Water

About 100 cm^3 of well mixed water samples were poured into a 150 cm^3 beaker. 5cm^3 of conc. HNO_3 was added. The solution was later evaporated to near dryness on hot plate, making sure that the sample did not boil by using low to medium heat. The beaker and contents was allowed to cool to room temperature before adding another 5 cm^3 conc. HNO_3 into the beaker. The beaker was immediately covered afterwards with a watch glass. The beaker was returned to the hot plate and set a gently reflux action of the solution by increasing the temperature of the hot plate (medium to high heat). We continued heating with the addition of conc. HNO_3 as necessary until light-coloured residue is obtained (i.e digestion is completed). Add 1-2 cm^3 conc. HNO_3 to the residue. Wash with distilled water. The solution was later filtered into 100 cm^3 volumetric flask to remove silicate and other insoluble materials and made up to the mark with distilled water in the volumetric flask. Store the solution in 125 cm^3 polypropylene bottle.

Analysis for Adsorption Using Oyster Shell Powder (OSP)

A setup was put in place where the separating funnel was mounted on a retort stand and below it, glass column chamber was also mounted to the stand, while a clean glass beaker was placed below the column chamber. The column chamber was filled with the oyster shell powder and then the separating funnel was opened and the produced water was allowed to run through the chamber filled with oyster shell powder into a clean glass beaker below, where the filtrate was collected. This procedure was carried out for the entire produced water sample, and was repeated, varying the pH of the oyster shell chamber. The concentrations of each of the metals were noted with AAS before and after injection in the column for the differences in concentrations of the respective metal in the produced water.

RESULT AND DISCUSSIONS

Table 1.0: Comparison of Nickel Concentrations (mg/L) in Produced Water Samples Before and After Filtration with Oyster Shell Powder at Different pH Levels

Sample	Initial Concentration	Filtered at pH 5.6	Filtered at pH 11.1
CC7T	0.116	0.097	<0.001
CC8T	0.708	0.645	<0.001
WELL 2 GSS	2.882	2.624	<0.001
WELL 8 TEB	0.254	0.200	<0.001
AZUZUAMA ST 1	0.076	0.202	<0.001
AZUZUAMA ST 2	0.438	0.392	<0.001

Table 2.0: Comparison of Cobalt Concentrations (mg/L) in Produced Water Samples Before and After Filtration with Oyster Shell Powder at Different pH Levels

Sample	Initial Concentration	Filtered at pH 5.6	Filtered at pH 11.1
CC7T	<0.001	0.008	0.009
CC8T	<0.001	0.010	0.013
WELL 2 GSS	0.026	0.070	0.488
WELL 8 TEB	0.049	0.119	0.681
AZUZUAMA ST 1	0.277	0.325	0.501
AZUZUAMA ST 2	<0.001	0.017	0.006

Table 3.0: Comparison of Copper Concentrations (mg/L) in Produced Water Samples Before and After Filtration with Oyster Shell Powder at Different pH Levels

Sample	Initial Concentration	Filtered at pH 5.6	Filtered at pH 11.1
CC7T	0.348	0.436	0.296
CC8T	0.549	0.690	0.481
WELL 2 GSS	0.195	0.262	0.155
WELL 8 TEB	0.274	0.345	0.232
AZUZUAMA ST 1	0.449	0.598	0.401
AZUZUAMA ST 2	0.392	0.565	0.289

Table 4.0: Comparison of Iron Concentrations (mg/L) in Produced Water Samples Before and After Filtration with Oyster Shell Powder at Different pH Levels

Sample	Initial Concentration	Filtered at pH 5.6	Filtered at pH 11.1
CC7T	7.194	2.416	<0.001
CC8T	52.692	22.148	<0.001
WELL 2 GSS	89.729	43.212	<0.001
WELL 8 TEB	2.785	0.102	<0.001
AZUZUAMA ST 1	24.578	10.218	<0.001
AZUZUAMA ST 2	5.372	1.031	<0.001

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Table 5.0: Comparison of Lead Concentrations (mg/L) in Produced Water Samples Before and After Filtration with Oyster Shell Powder at Different pH Levels

Sample	Initial Concentration	Filtered at pH 5.6	Filtered at pH 11.1
CC7T	0.277	0.170	<0.001
CC8T	0.483	1.282	<0.001
WELL 2 GSS	<0.001	0.200	<0.001
WELL 8 TEB	<0.001	0.221	<0.001
AZUZUAMA ST 1	0.213	0.571	<0.001
AZUZUAMA ST 2	0.013	0.389	<0.001

Table 6.0: Comparison of Calcium Concentrations (mg/L) in Produced Water Samples Before and After Filtration with Oyster Shell Powder at Different pH Levels

Sample	Initial Concentration	Filtered at pH 5.6	Filtered at pH 11.1
CC7T	71.751	178.219	55.214
CC8T	66.176	160.001	48.129
WELL 2 GSS	16.217	43.723	7.626
WELL 8 TEB	92.714	276.240	78.281
AZUZUAMA ST 1	61.654	157.428	50.142
AZUZUAMA ST 2	82.616	220.299	71.427

Table 7.0: Comparison of Potassium Concentrations (mg/L) in Produced Water Samples Before and After Filtration with Oyster Shell Powder at Different pH Levels

Sample	Initial Concentration	Filtered at pH 5.6	Filtered at pH 11.1
CC7T	98.970	115.996	117.413
CC8T	100.444	121.001	121.428
WELL 2 GSS	96.386	114.877	116.380
WELL 8 TEB	100.389	120.820	120.478
AZUZUAMA ST 1	103.965	125.424	122.319
AZUZUAMA ST 2	105.416	129.721	124.143

DISCUSSIONS

Effect of pH Value on metal adsorption

Results of the effect of pH on metal adsorption by the Oyster shell are shown from Tables 1.0 and 7.0. To study the influence of pH on the bio-sorption of Nickel (mg/L), Cobalt (mg/L), Copper (mg/L), Iron (mg/L), Lead (mg/L), Calcium (mg/L) and Potassium (mg/L)batch experiments were carried out at different pH values (from 5.6 to 11.1) for all metals. The amount of heavy metal ions adsorbed onto OS was sensitive to pH variations in the test range of 5.6≤pH≤11.1. The amount of heavy metal ions adsorbed increased as the pH rose from 5 to 11 and reached maximum at 6≤pH≤8. Overall, metal adsorption by OS increases with an increase in solution pH. In general, the removal efficiency of OS and initial metal concentration decreased with an increase in the solution pH (from acidic to basic solution).

Comparison of Metal Concentrations in Produced Water Samples Before and After Filtration with Oyster Shell Powder at Different pH Levels

The initial and filtered concentrations of metals (Nickel, Cobalt, Copper, Iron, Lead, Calcium, and Potassium) in produced water samples treated with oyster shell powder at different pH levels (5.6 and 11.1) are presented in tables 1.0 – 7.0.

The treatment with oyster shell powder at pH 11.1 was highly effective for Nickel removal, with concentrations dropping below detectable levels across all samples, indicating complete adsorption. In contrast, filtration at pH 5.6 showed only moderate reductions, suggesting the higher pH significantly enhances Nickel adsorption.

For Cobalt, the initial concentrations were mostly below the detection limit, except for WELL 2 GSS and AZUZUAMA ST 1. After filtration at pH 5.6, the Cobalt levels increased slightly in all samples. Filtration at pH 11.1 resulted in higher Cobalt concentrations than the initial and pH 5.6 treatments, indicating that the higher pH might be causing Cobalt to leach from the oyster shell powder or that the adsorption medium is not effective for Cobalt at high pH levels.

The Copper concentrations initially ranged from 0.195 mg/L in WELL 2 GSS to 0.549 mg/L in CC8T. Filtration at pH 5.6 led to an increase in Copper concentrations, whereas at pH 11.1, the concentrations were reduced but not significantly, suggesting that oyster shell powder may not be very effective for Copper adsorption, and higher pH might slightly enhance the adsorption efficiency.

Iron concentrations were initially very high, especially in WELL 2 GSS and CC8T. Filtration at pH 5.6 resulted in significant reductions in Iron concentrations, and at pH 11.1, the Iron concentrations dropped below detectable levels in all samples, indicating that oyster shell powder is highly effective for Iron removal, particularly at higher pH levels.

Lead concentrations were initially low or below the detection limit in most samples. Filtration at pH 5.6 led to variable results, with some samples showing an increase in Lead concentrations. However, at pH 11.1, Lead concentrations dropped below detectable levels in all samples, demonstrating that higher pH significantly enhances Lead adsorption.

Calcium concentrations were initially high across all samples. Filtration at pH 5.6 led to a significant increase in Calcium concentrations, suggesting desorption or leaching from the oyster shell powder. At pH 11.1, Calcium concentrations were reduced compared to the initial levels, indicating that higher pH might stabilize Calcium adsorption or prevent desorption.

Potassium concentrations were initially high, around 100 mg/L. After filtration at both pH levels, there was an increase in Potassium concentrations in all samples. This suggests that the oyster shell powder is not effective for Potassium adsorption and may even contribute to increased Potassium levels in the treated water.

The results obtained from the laboratory analyses to determine the concentrations of some heavy metals in the produced water contained traces of metals. These values are comparatively higher than the tabulated heavy metal limits for effluent limitations for Inland/Near shore oil and gas installations for oily waste water by the EGASPIN (2018). The current study established that the levels of Nickel (mg/L), Cobalt (mg/L), Copper (mg/L), Iron (mg/L), Lead (mg/L), Calcium (mg/L) and Potassium (mg/L)in produced water were below the limits (except for Nickel and Iron) set by EGASPIN (2018).The public health concern in terms of produced water in Nigeria's industrial area is therefore Fe and Ni levels which were above the limits set by (EGASPIN, 2018). This finding aligns with the report of Al-Othman and Naushad (2011). Aljendeel (2011), reported higher levels of Fe in produced water which aligns with the present study. The concentration of parameters investigated trend as follows K>Fe>Cu>Ca>Co>Ni>Pb. Result indicates that Fe and Ni are well above the regulatory limit which could be of pollution effect through runoff into surface water or by percolation into groundwater. In the current study areas, humans can become exposed to such pollutants when surface runoffs find their way into residential areas or utilizing the contaminated water for agricultural activities. Clogging of open waste water channels with solid wastes, mud and overgrown vegetation can enhance surface runoff of the produced water to surrounding areas. One of the factors which may increase the chance of exposure to metal pollutants in the study area is presence of a dense population in the informal settlements (Djedidi et. al. (2009); EPA (1990); Iwuoha et. al. (2012).

Heavy metals are a known cause of long-term health effects in humans. Such effects include not only nefarious effects of acute and/or chronic toxicity, but also special cases of toxicity such as carcinogenicity and genotoxicity. Heavy metals are major pollutants because of their toxicity, their persistence and, their tendency to bioaccumulate in the food chain. They represent a risk for aquatic ecosystems and humans, Igwe et. al. (2020).

Produced water has been established to contain certain heavy metals. Most heavy metals are well-known toxic and carcinogenic agents and represent a serious threat to the human population and the fauna and flora of the receiving water bodies (Irani et al., 2011). Heavy metals have a great tendency to bio-accumulate, end up as permanent additions to the environment and have a detrimental effect on human health Jha et. al. (2009). However, differences in the type, concentration, and chemical content of the metals are influenced by the geological age and features, and the injected water volume. Adsorption potentials of metal ions from produced water using oyster shells were investigated with respect to contact time. Contact time has been established to be a significant influential factor that could affect adsorption efficiency, and the test results could be used to confirm the equilibrium time and describe the adsorption kinetics Nkanga et.al.(2024); Kabwadza-Corner et.al. (2014); Lee et. al. (2000); Lin and Navarro (1999).

CONCLUSION

The results indicate that adjusting the pH value of adsorbent medium to 11.1 was excellent in removal of total Nickel, Iron and Lead from produced water, while adjusting the pH of the (OS) adsorbent medium to about 5.6 was less effective in removing or reducing above metals and their ions concentrations in produced water. Adjusting the pH value between 5.6 and 11.1 was totally ineffective and did not reduce the concentration of total Calcium, Copper, Calcium and Potassium in the produced water, however it increased in some of above noted metal due to reasons given before now. Other recovery and remediation techniques like Detoxification by chemical reaction technology should be understudied and their recovery efficiency, cost effectiveness and environmental friendliness compared with above method.

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