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Research Article

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Treatment of Surface Water Using Multiple Barrier Technique

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ABSTRACT
Surface water was treated using the Multiple Barrier Technique comprising calcite, marble, and limestone in a bucket fitted with a tap. Water samples were collected from the principal water source for Ambrose Alli University – Ibiekuma River in Ekpoma. The following physicochemical parameters – Total Solids (TS), Total Dissolved Solids (TDS), Suspended Solids (SS), Turbidity, and pH – were used to evaluate the raw water and monitor the treatment process. The results obtained showed how the interaction with the mineral barriers moderated these parameters over time, with SS (0.56 mg/l), TDS (3.89 mg/l), TS (4.45 mg/l), and turbidity (0.003 NTU). The study revealed that the pH of the river water is mildly acidic (4.82), which was immediately moderated to 7.76 upon contact with the barriers. While the analysis of the mineralogical constituents of the water was not conducted, the results capture the effectiveness of the barrier in stabilising pH, maintaining low turbidity, and releasing minerals into the water, enhancing its mineral profile without exceeding safe limits for domestic, agricultural, and industrial use as defined by the World Health Organization (WHO) and the Standards Organization of Nigeria (SON). This study demonstrated the potential of this barrier system as a sustainable and cost-effective alternative to synthetic chemicals for water treatment.

Keywords: Calcite, Limestone, Marble, Physicochemical Parameters, Surface Water, Water Treatment

Introduction

The availability of sufficient and uncontaminated water for household use in rural areas remains an issue that affects many people in developing countries [1]. Access to clean and safe water has been a persistent challenge in Nigeria. Many rural communities have solely relied on roof-harvesting rainwater, stored in underground reservoirs, as their primary source of water for drinking and domestic use across the country [2-4]. In Edo State, Nigeria, particularly in Ekpoma, which is the administrative headquarters of Esan West Local Government Area, where quality water has been a major issue, predominantly relies on roof-harvested rainwater stored in underground reservoirs. The town's geological features negatively impact the availability of groundwater in the region [5-7]. This is primarily influenced by seasonal changes, with variations in rainfall and surface water sources. This impacts the level of pollutants in the water consumed by the community [8,9]. Despite the glaring problems of water scarcity in Nigeria, little attention is given to evaluating the condition of rainwater harvesting systems. This continues to impact the health of many rural communities, with reports of high neonatal and infant mortality due to diarrheal diseases, particularly in Edo State, where roof-harvested rainwater is a prevalent practice [10-12]. Herein, we report the evaluation of water parameters based on the principle of adsorption, using natural minerals: limestones, calcites, and marbles.

Mineral Materials

Calcite

Calcite, with the chemical formula $CaCO_3$, is found in a wide range of rocks. It is the principal constituent of limestone and marble. It is usually white but also colorless, grey, red, green, blue, yellow, brown, or orange, and is the world's most abundant mineral after quartz [13,14]. It decomposes upon heating to form quicklime and carbon dioxide and reacts with water to form slaked lime (limewater).

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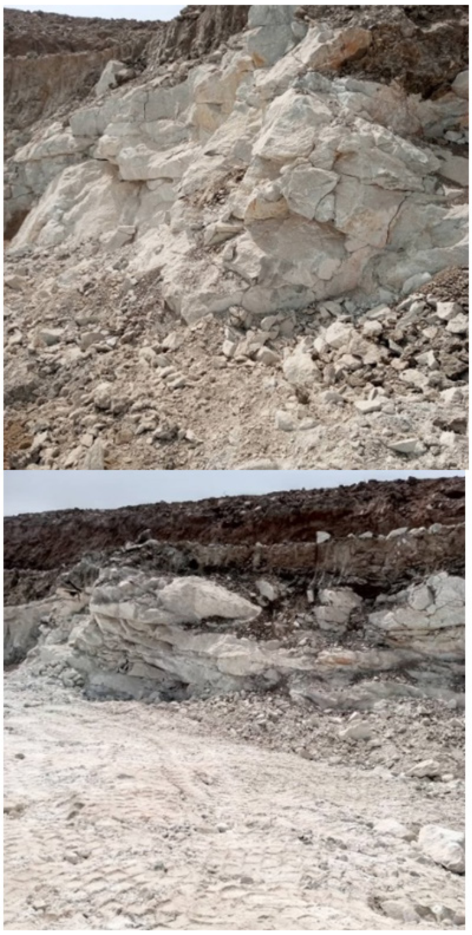

Figure 1: Pictures of calcite deposit at BUA cement Company Ltd, Obhu-Okpella quarry.

Limestone

Limestone is composed of both calcite and aragonite, which are different forms of calcium carbonate ($CaCO_3$) [15]. It forms either through precipitation due to biological activity or through direct precipitation due to inorganic processes [16]. It is typically grey, but it can range in color from white to black. Most freshwater and seawater contain dissolved calcium carbonate, which crystallizes out of solution, due to temperature or pH changes, to form limestone. It is also formed by the biological accumulation of skeletons and shells of marine organisms, such as sea urchins and coral, over time. Limestone, which is composed of $CaCO_3$ contains the carbonate radical (CO_3^{2-}) [17]. It consists of varying amounts of calcium carbonate, magnesium carbonate, silica, alumina, ferric oxide, sulfate, phosphorus, potash and soda, with calcium and magnesium carbonate as the primary components [18]. Its high porosity, or percentage pore space in its total volume gives it a relatively faster rate of calcination and a more reactive quicklime [19]. These properties make it a very good adsorbent.

Marble

Marble, a metamorphic rock, is formed when limestone undergoes intense heat and pressure, which alters its structure and mineral composition. Under the influence of heat and pressure (metamorphism), the limestone re-crystallizes into interlocking calcite crystals, to form marble. It is typically a light-colored rock and appears white when formed from limestone with few impurities. Composed mainly of carbonate minerals like calcite ($CaCO_3$) or dolomite ($CaMg(CO_3)_2$), it also contains other minerals like clay, graphite, pyrite, quartz, iron oxide, and micas. It forms carbonate ions (CO_3^{2-}), which can neutralize acids when it gradually dissolves in water [20,21].

Figure 2: A picture of the marble deposit at BUA Cement Company Ltd, Obhu-Okpella quarry.

Decomposition and Hydrolysis

$$CaCO_3 \rightarrow \underset{\text{Quicklime}}{CaO} + CO_2$$

$$CaO + H_2O \rightarrow \underset{\text{Lime water}}{Ca(OH)_2}$$

Pollution

Pollution occurs when unwanted materials accumulate in areas where they disrupt natural processes, and it has become evident that these pollutants pose serious risks to both the environment and public health [1]. Water's natural ability to dissolve and carry materials allows it to be easily contaminated by human activities. A water contaminant is any physical, chemical, biological, or radiological substance or matter in water [22,23]. Nigeria, the most populous Black nation on Earth, possesses abundant surface and groundwater resources, but the supply of clean and safe drinking water remains insufficient [24]. Due to the growing population, the level of pollution continues to increase continuously from urban to rural areas. These concerns prompt a continuous effort to develop cost-effective water treatment methods that can remove or neutralize harmful pollutants, particularly in rural areas [25]. Various filtration and treatment technologies, including those that focus on the removal of organic matter, toxic substances, and micro-pollutants, are critical for ensuring water safety and preventing further environmental degradation. The two major surface water sources in the town are the River Ile and Ibiekuma River, with the latter serving as the primary source of water for Ambrose Alli University. Recent studies on surface water treatment show how innovative technologies have been explored to improve the removal of various contaminants and the overall quality of water. An example of such an approach reviewed the combination of limestone filtration and ultrafiltration, as well as other natural adsorbents [26].

Water Treatment Process

Water treatment requires chemical, physical, and biological processes to remove contaminants. The chemical processes include coagulation and disinfection. The physical processes include flocculation, sedimentation, filtration, and adsorption. The type of process employed and the order in which they are used depend on the quality of the water supply [27,28].

Coagulation and Flocculation

Coagulants such as ferric chloride ($FeCl_3 \cdot 6H_2O$), aluminum sulfate ($Al_2(SO_4)_3 \cdot 18H_2O$), and aluminum chloride ($AlCl_3$) are widely used to remove fine particles, sediments, and impurities in water. These chemicals work by destabilizing colloidal particles and facilitating their aggregation into larger flocs, which are easier to remove [29]. However, their environmental impact and health hazards have increased continuous interest in exploring sustainable alternatives. For instance, Moringa oleifera has been explored to address sustainability and has proven its effectiveness as a natural coagulant [30-33]. Starches from agricultural products like wheat, potato, and corn have also offered promising alternatives to traditional coagulants in water treatment [34,35].

Adsorption

Adsorption involves the migration of particular fluid or gaseous phase components onto a solid-phase surface [36]. In this process, specific elements from the fluid or gaseous phase are captured and bound to the solid phase for separation to occur. It is a crucial process in the purification of water. The mechanism entails the clumping of substances in a liquid or gaseous phase (absorbate) at the interface of another material (adsorbent). These phases may be, liquid-solid, gas–liquid, or gas-solid interfaces. The effectiveness of adsorption processes is influenced by the solid-liquid interactions and the speed at which molecules move between the two phases [37,38]. Researchers have explored different kinds of adsorbents, such as gravel, charcoal, plants, stones, etc. For instance, charcoal has been reported to be an efficient filtration medium [39,40]. Gravel and charcoal have also been commonly used as a medium for filtration due to their availability and proven performance in sedimentation and turbidity reduction processes [41]. Gravel has been a very reliable medium, but incorporating charcoal has proven to enhance filtration efficiency, particularly in settings where higher turbidity removal or adsorption of organic materials is necessary. Studies reveal that charcoal acts as a better adsorbent than gravel, with its adsorption capacity playing an important role in its superior performance compared to traditional gravel media [24]. Similarly, limestone has previously been reported to be particularly effective for treating wastewater. It has high efficiency in treating sulfate concentrations below 1200–2000 mg/L, a range where lime precipitation methods are less effective [26,42]. Its soft texture makes it an effective adsorbent. Geological surveys show that limestone is highly soluble, which allows it to gradually dissolve in water, and the longer it is subjected to the forces of nature, the more porous it becomes [43].

Objective and Aim

The objective of this study was to obtain water samples from the Ibiekhuma River using the grab sampling method, collect mineral materials such as calcite, marble, and limestone, assemble a water treatment reactor using these mineral materials in a plastic bucket fitted with a tap, and to contact the mineral materials with water to monitor the following physicochemical parameters: pH, turbidity, suspended solids, total dissolved solids, and total solids for both the raw and treated water samples. The overall aim was to treat water using a composite unit of calcite, marble, and limestone in a reactor.

Theoretical Analysis

Determination of Suspended Solids

Calculation

$$SS\ (mg/L) = \frac{(Wt_A - Wt_B) \times 1000}{\text{Vol. of aliquot}}$$

Wt_A = Weight of filter paper after filtration, Wt_B = Weight of filter paper before filtration

Determination of Total Dissolved Solids

Calculation

$$SS\ (mg/L) = \frac{(Wt_{DR} - Wt_D) \times 1000}{\text{Vol. of aliquot}}$$

Wt_D = Weight of dish; Wt_{DR} = Weight of dish + dried residue

Determination of Total Solids

TS (mg/L) = SS + TDS

Experimental Section

Assemblage of the Water Treatment Reactor

A transparent High-Density Polyethylene (HDPE) bucket with upper and lower circumferences of 32 cm and 22 cm, respectively, and a height of 32 cm, was acquired. A tap was fitted at the bottom edge of the bucket, as shown in Figure 3. Cotton wool was inserted into the fitted tap to serve as a filter. This helps to reduce the number of solid particles passing through the tap during sample collection.

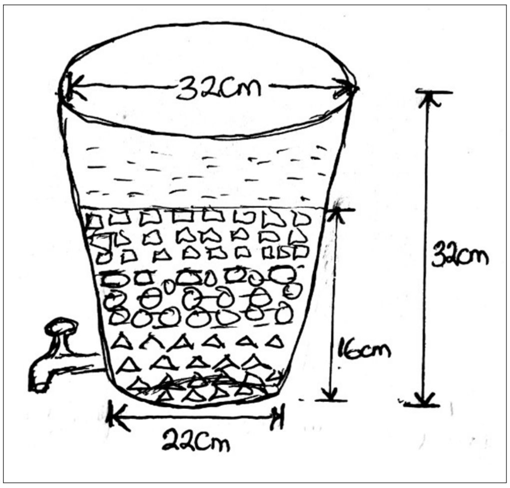

Figure 3: Dimension of the water treatment reactor

Study Area

The study was conducted on the Ibiekuma River in Ekpoma, located in the Esan West Local Government Area of Edo State, Nigeria. The river flows through the dense forest of Ujemen behind Ambrose Alli University, approximately 5 km from the campus. Ekpoma generally lacks reliable water sources, as there are no functional boreholes or well water due to its geographical location (coordinates: latitude 6°45′N, longitude 6°08′E). It is a fast-growing town with a land mass of 502 km² and a population of 190,000 people [44].

Sampling

Following the methods outlined by the American Public Health Association and the Government of Western Australia [22,45], a grab sample of surface water from the Ibiekuma River was collected in a 25-litre plastic bottle. The bottle was prewashed with distilled water and rinsed several times with the sample water before collection. The water was carefully collected directly into the sampling bottle to ensure that the bottom sediment or aquatic plants were not disturbed, as this could increase turbidity. The sample was immediately transferred to the laboratory for analysis. The mineral materials that constituted the barrier, whose geochemistry had previously been characterized were obtained from different locations in Nigeria [20,46]. The highly fossiliferous limestones were collected from LaFarge Cement Company, Ewekoro deposit, Sabo, Ogun State (Shagamu quarry), while the marble and calcite were collected from BUA Cement Company, Obhu-Okpella, Edo State (Obhu quarry).

Sample Preparation

The mineral materials were broken into pieces approximately ¼ inch in size, then washed several times with water until they were clean. They were soaked in water overnight, drained with clean water the next day, and allowed to dry for thirty minutes. Distilled water was added to the mineral materials for another thirty minutes, after which they were drained. The barriers were then transferred to the treatment reactor in the order of limestone, marble, and calcite (5 cm: 5 cm: 6 cm), as shown in Figure 4.

Figure 4: A complete setup of the treatment reactor

The water sample was transferred into the reactor up to the 21-litre mark. A 50 mL aliquot was taken and analyzed for raw water for each of the parameters. After the first hour, another 50 mL aliquot was collected through the tap and analyzed for each of the parameters. This was repeated after the 2nd, 3rd, 19th, 22nd, and 24th hours of treatment, respectively.

Procedures

Determination of pH

The meter was first calibrated with buffers 4, 7, and 9. The pH of the raw water was measured and recorded. This process was repeated after the 1st, 2nd, 3rd, 19th, 22nd, and 24th hours of treatment, and the values were recorded accordingly.

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Determination of Turbidity

A UV spectrophotometer was used to measure the turbidity at a wavelength of 860 nm. The spectrophotometer was calibrated using a standard solution with known turbidity values (formazin solution). An aliquot of the raw sample was pipetted into a cuvette and placed in the spectrophotometer to measure the absorbance. The readings were taken and recorded. The same procedure was repeated after the 1st hour of treatment and during the subsequent hours. A calibration curve was created using the standard solution with known NTU values to determine the turbidity readings in NTU.

Determination of Suspended Solids

A Whatman filter paper (110 mm) was weighed and used to filter 50 mL aliquot from the raw sample into a beaker. The wet filter paper was transferred to an oven and dried at a temperature of 105 ºC for an hour. It was then cooled in a desiccator and weighed to a constant weight. The same procedure was repeated after the first hour of treatment and during the subsequent hours. The weights were recorded accordingly in each case.

Determination of Total Dissolved Solids

An evaporating dish was washed with distilled water, dried in an oven for five minutes at a temperature of 105 ºC, cooled in a desiccator and weighed. A 50 mL aliquot was taken from the raw sample, filtered into the evaporating dish using Whatman filter paper (110 mm), and dried at 105 ºC for an hour. The dish was then cooled in the desiccator, weighed to a constant weight, and the weight was recorded. The same procedure was repeated after the first hour of treatment and during the subsequent hours. The weights were recorded accordingly in each case.

Determination of Total Solids

The sum of the concentration of SS and TDS accounted for the concentration of the TS of each sample at regular times.

Results and Discussion

The results capture the effectiveness of the barrier in stabilizing pH, maintaining low turbidity, and releasing minerals into the water to enhance its mineral profile without exceeding safe limits for any parameter. Water pH is an indication of its acidic or basic nature. pH is an important parameter in potable water, which influences its quality, as it affects the solubility of metals, hardness, and alkalinity. As shown in Table 1, the river water was mildly acidic (pH 4.82), which failed to meet the minimum requirement for potable water.

Table 1: Values of physico-chemical parameters for the raw and treated water samples.

Physicochemical parameters	Time of analysis (hours)								WHO Standard
	Raw	1st	2nd	3rd	19th	22nd	24th	Average	
pH	4.82	6.47	8.03	8.16	8.03	7.98	7.90	7.76	6.5 – 8.5
Turbidity (NTU)	0.046	0.055	0.055	0.054	0.050	0.050	0.050	0.003	< 1NTU
SS (mg/L)	0.276	0.076	0.42	0.20	1.284	0.624	0.768	0.56	≤ 25mg/l
TDS (mg/L)	0.22	1.804	0.328	1.066	6.806	7.790	5.538	3.89	≤ 25mg/l
TS (mg/L)	0.496	1.88	0.748	1.266	8.09	8.414	6.306	4.45	≤ 500mg/l

Upon contact with the barriers (mineral materials), the pH was immediately moderated and stabilized between the 2nd and 24th hours, remaining within WHO standard limits of 6.5 – 8.5 [47]. This indicates the successful buffering capacity of the barriers, primarily due to the dissolution of calcium carbonate ($CaCO_3$) from limestone, calcite, and marble. The $CaCO_3$ neutralized the acidity by releasing bicarbonate ions. Figure 5 illustrates the stability of the pH over time.

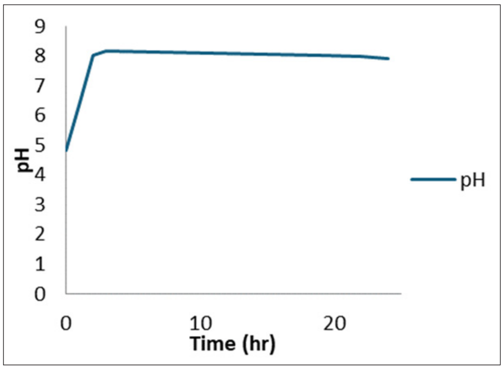

Figure 5: A graph of pH vs Time (hr)

The low turbidity-maintained shows that the materials did not introduce significant particulate matter into the water, as the turbidity remained low within the recommended limit (< 1 NTU) throughout the process, as shown graphically in Figure 6. This shows that the materials (calcite, marble, and limestone) do not dissolve or erode significantly in water and no fine particles or sediments are released to cloud the water.

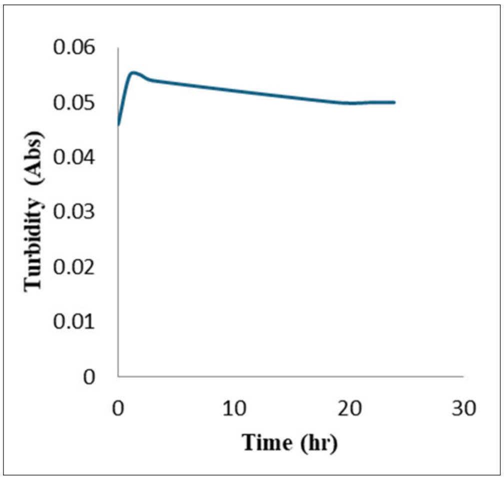

Figure 6: A graph of turbidity vs time (hr)

It was observed that the suspended solids (SS) peaked at the 19th hour, corresponding to the maximum erosion of fine particles from the barrier. This occurred because the filtration system attached to the tap on the treatment reactor had relatively large pores, which allowed suspended particles to pass through. This issue can be controlled during reactor assembly by increasing the quantity of cotton wool used to pre-filter the sample during collection. However, a drastic decrease was observed from the 22nd hour, which corresponds with the progression from the 1st hour. The high peak at the 19th hour may also be attributed to a possible disturb of the reactor. The total dissolved solids (TDS) increased progressively due to the dissolution of calcium and other minerals from the barriers, remaining within the WHO safety limit for potable water (≤ 25 mg/L) [47]. The components of the barrier exhibited their efficiency in improving water quality by striking a balance between mineral dissolution (increasing TDS and TS) and stabilization. We see the influence of SS and TDS on the TS as it also increased proportionately to these parameters. All measured parameters remained within the safety limits for domestic, agricultural, and industrial use as defined by the WHO and SON [47-49].

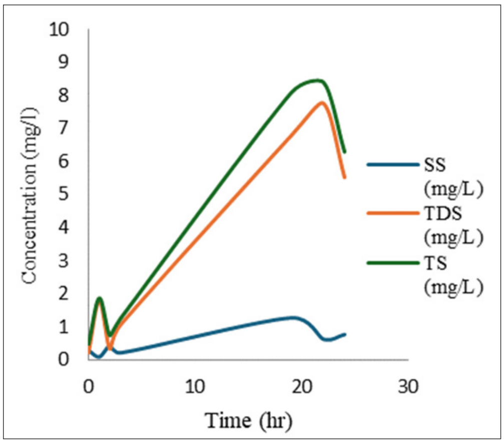

Figure 7: A graph of SS, TDS, TS (mg/L) vs Time (hr)

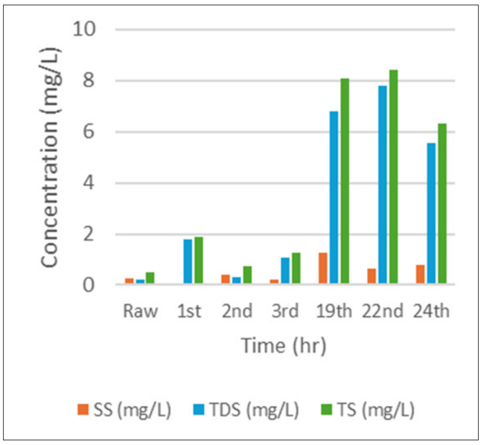

Figure 8: Graphs of SS, TDS, and TS (mg/L) vs Time (hr)

Conclusion

This study demonstrated a practical and sustainable method to improve water quality in Ekpoma by addressing challenges, such as geological constraints and reliance on rainwater. The multiple barrier system confirmed that the minerals actively modify water chemistry, not just filteration, through an effective pH stabilization. This indicated that the buffering capacity of the minerals is just enough to to raise pH without over-saturating the water. This reduces corrosion risks and toxic metal leaching from pipes as well as irritation risks (skin, eyes) from hilghly acidic water. The consistent low turbidity confirmed that the materials pose no risk of secondary contamination. The materials also proved a contribution to water hardness without exceeding safe limits for any parameter. It is recommended that potable water should contain a specific amount of hardness as it provides essential minerals like calcium and magnesium, important for bone health and various bodily functions. This report shows that this treatment process can be used to regulate the concentration of dissolved and suspended particles in water. The persistent use of synthetic chemicals in water treatment poses a growing threat to human health. Sustainable practices, such as incorporating natural coagulants and reusing water treatment residuals, afford environmentally benign and cost-effective alternatives. The application of mineral materials such as calcite, marble, and limestone in a multiple-barrier system reduces dependence on synthetic chemicals as well as the threats pose by these chemicals to human health. These materials are locally accessible and provide an affordable alternative to expensive treatment systems.

Recommendation

This treatment method is effective and aligns with WHO standards for potable water To further minimize variability in suspended solids, improvements in sedimentation or filtration steps, such as increasing the cotton filter size in the tap or incorporating settling tanks, are recommended. Additional optimization could involve studying the dissolution kinetics of the materials to predict and control pH stabilization and changes in solid content over time.

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Ethical Statement

This study does not contain any studies with human or animal subjects performed by any of the authors.

Conflict of Interest

The authors declare no conflict of interest

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