



Treatment of Iron Rich Groundwater Using KMnO_4 and a Fixed Bed of Animal Bone Char

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Author's contribution

This whole work was carried out by author ARR.

Original Research Article

Received 12th April 2014
Accepted 18th May 2014
Published 2nd June 2014

ABSTRACT

The chemical composition of groundwater samples in Yenagoa, Bayelsa State of Nigeria was experimentally investigated. Parameters as pH, temperature, redox potential, iron oxidizing bacteria, dissolved oxygen, iron and manganese were analysed. Results indicate the groundwater samples are rich in iron (3.28mg/L) above regulatory limits of 0.3mg/L. A treatment process was developed to improve the quality of the groundwater. The treatment process involves pre-treatment of the effluent with varying concentrations of KMnO_4 (1.5mg/L, 2.0mg/L and 2.5mg/L), and passed through a fixed-bed of bone char. The treatment process involving the use of 2.5mg/L dose of KMnO_4 filtered through a fixed bed of bone char treatment showed iron and manganese reduction from 3.28mg/L to nil and from 1.03mg/L to nil representing 100% reduction for both metals. Iron oxidizing bacteria (IOB) was reduced from 10^6 cfu/ml to 10^1 cfu/ml reduction representing 99.999% reduction. Values of pH, temperature, dissolved oxygen (DO) and redox potential were also affected. Results showed a good compliance with World Health Organisation (WHO) standards for drinking water. This means that the final effluent obtained is safe for human consumption and poses no aesthetic nuisance.

Keywords: Groundwater; iron-rich; bone char; potassium permanganate; fixed-bed.

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1. INTRODUCTION

Groundwater is water located beneath the earth's surface in soil pore spaces and in the fractures of rock formations called aquifer. An aquifer is a unit of rock or an unconsolidated deposit that yields a usable quantity of water. Groundwater resources play a vital role in the production of clean and adequate drinking water supply all around the world. In most urban cities in Nigeria, groundwater is a major source of drinking water [1]. In European countries, like Denmark, Austria and Iceland, more than 95 percent of their water supplies originate from groundwater reservoirs [2]. In the United States, groundwater is used to supply potable water for more than 96 percent of their population in rural areas [3]. In Asia, groundwater is also used extensively for their water supplies e.g. 80 percent in (rural) india, 80 percent in Maldives and more than 60 percent of water supply in Philippines and Nepal originates from groundwater resources [4].

The extensive use of groundwater may stem from the fact that it is of a higher water quality compared to surface water [5]. This is as a result that soil is a natural filter where processes such as filtration, adsorption, biodegradation, ion exchange and dispersion may reduce concentration of contaminants to a great extent [6,7]. In addition, ground water is less subject to seasonal and perennial changes, uniformly spreading over large areas [8] and also lower capital cost of production [4]. These benefits have resulted in groundwater use for water supply at large scale [8].

Water is a universal solvent, carrying with it a lot of organic and inorganic impurities that it is in contact with. The chemistry of groundwater varies from place to place depending on the nature of the subsoil and rocks that it passes through. It has been observed that in areas where limestone bedrock and limestone-dominated subsoil are common, groundwater is often 'hard', containing high concentrations of calcium, magnesium, and bicarbonate [9]. However, in areas where volcanic rocks of sandstones are present, softer water is normal. Generally, major contaminants found the groundwater include sulphates, nitrogen compounds (such as ammonia and nitrates, petroleum products, phenols and heavy metals [8]. Other contaminants found in groundwater are naturally occurring heavy metals such as magnesium, calcium, iron and manganese [10]. Iron and manganese have been causing problems for regulatory authorities in connection to industrial and main water supplies for a long time [11]. Higher dissolved concentrations of iron and manganese do not have any serious harm to human or animal health [12], but these can cause aesthetic problems [10]. Iron dissolved in groundwater delivered via domestic water systems can produce unsightly rust stains on above ground storage tanks, buildings, paths, fences and plants in many areas. It may also stain clothes washed in iron-rich water and plumbing fixtures such as basins and toilet bowls. These rust stains resist cleaning with soaps, detergents and bleach.

Water should ideally be drawn from a source that has a low iron concentration (typically less than 1mg/L). These waters are normally neutral to alkaline and contain some dissolved oxygen. When iron is present in water as soluble form in drinking water supplies, then we will come across many objectionable problems related to their presence. The World Health Organization (WHO) has approved the removal of iron when concentration is higher than 0.3mg/L [13]. European Union has recommended the levels of 0.2mg/L for iron [14]. The Environmental Protection Agency (EPA) has established secondary standards of 0.30mg/l for iron [15]. So if concentrations are higher than these standards, then water must be treated before using it for drinking purposes. If water is not treated then there can be different problems for water consumers and also for that municipality that delivers drinking water to consumers.

Treatment of water samples especially removal of iron and reduction of some physico-chemical properties has been widely studied over the last decade [16,17,18]. However, the need to develop effective treatment methods has become more pressing with the ever-tightening restrictions on effluent quality and increased community awareness in recent years. Potassium permanganate (KMnO_4) has been used as a coagulant to produce a heavier floc with greater settling velocity [19]. Bone char is noted to be a cheap material and the ability of bone char to adsorb a considerable amount of metal ions has been demonstrated [20]. This study investigates a treatment method using KMnO_4 as a coagulant passed through a fixed bed filled with bone char to improve the groundwater quality in the study area. A preliminary assessment of the iron content of the groundwater samples in the study area showed that its value is above permissible levels for drinking purposes hence the need for this study.

2. MATERIALS AND METHODS

2.1 Study Area

The study area is Yenagoa which is a Local Government headquarter of Yenagoa Local Government Area in Bayelsa State, Nigeria (Fig. 1). Yenagoa is also the capital city of Bayelsa State. It is located in the Niger Delta area of Nigeria with a geographical coordinate of $4^{\circ}55'29''\text{N}$ and $6^{\circ}15'51''\text{E}$. The LGA has an area of 706km^2 and a population of 353,344 at the 2006 [21].



Fig. 1. Map of Nigeria Showing the Study Area

The study area is part of the Sombreiro Warri Deltaic plains which consists of brownish grey fine sand, silt, clay and mangrove swamps of the Quaternary age. The Sombreiro Warri Deltaic plain is underlain by the Benin Formation, which extends from the west across the whole Niger Delta area and southward beyond the present coastline. The Benin Formation is itself underlain by the Agbada formation. Bayelsa State is located within the lower delta plain believed to have been formed during the Holocene of the quaternary period by the

accumulation of sedimentary deposits. The major geological characteristic of the state is sedimentary alluvium. The entire state is formed of abandoned beach ridges and due to many tributaries of the River Niger in this plain, considerable geological changes still abound [22,23].

Previous study of the meteorology of the area [24], reveals the average atmospheric temperature to be 25.50°C in the rainy season and 30.00°C in the dry season. The daily relative humidity values range from 55.50% in dry season to 96.00% in rainy season. Rainfall in the area averages 2,500mm annually. The rainfall pattern shows two identifiable seasons: the rainy season (April to October) and the relatively short dry season (November to March).

2.2 Bone Char

Bone char used for the study were prepared by burning animal (Cow) bones collected from an abattoir in Yenagoa. The use of animal bone char in the treatment of water is purposed to solve two environmental problems: improving the quality of drinking water in the study area and the management agricultural waste arising from heaps animal slaughter waste. The bones were subjected to an elevated temperature of about 180°C for 10 hours in an oven. The charred bones were cooled to room temperature. They were then pulverised to fine particles using a laboratory grinder and sieved through a 5mm mesh. Chemical and physical characteristics of bone char as presented in Table 2 have been reported [25].

2.3 Preparation of $KMnO_4$

Potassium permanganate ($KMnO_4$) is used primarily to control taste and odors, remove colour, control biological growth in treatment plants, and remove iron and manganese [19]. A primary use of permanganate is iron and manganese removal. Permanganate will oxidize iron and manganese to convert ferrous (2+) iron into the ferric (3+) state and 2+ manganese to the 4+ state. The oxidized forms will precipitate as ferric hydroxide and manganese hydroxide. For the purpose of this study, varying concentrations of 1.5mg/L, 2.0mg/L and 2.5mg/L of $KMnO_4$ were prepared using standard method [26]. The prepared doses are appropriate for iron oxidation [27].

2.4 Groundwater Samples Collection and Analysis

In the study area, three groundwater storage tanks were randomly selected. The choice of the groundwater storage tanks was as a results of unsightly rust stains seen on the external body of the tanks. At each of the identified site, groundwater sample was collected collected in a labeled 2.5L plastic sample container that has been pre-treated by washing in dilute HCl and rinsed with distilled water. At the collection point, containers were rinsed with relevant water sample twice. Collected samples were taken to the Federal University of Petroleum Resources, Department of Environmental Science Laboratory for analysis. Samples were analysed for, pH, temperature, dissolved oxygen, redox potential, iron oxidising bacteria (IOB) – lepthrothrix discophora, managanese and iron. These parameters are good environmental impact indicators for iron pollution studies [28]. Fast changing parameters such as; pH, temperature, dissolved oxygen (DO), were measured *in-situ* using a multi-parameter water quality (model 600 UPG). Note that the multi-parameter water quality monitor was properly checked and calibrated before and after use. Redox potential was

measured *in-situ* using Orion multimeter (model 1260) and combined platinum / silver (silver chloride electrodes).

Iron and manganese content of the samples was determined using ATI Unicam Atomic absorption spectrophotometer, model 939.

The population of iron oxidising bacteria of samples was determined using the rapid agar dipstick method. The choice of the rapid agar dipstick method is based on its ease of application and reliability; it can be used on site and is widely reported in literature [29-33]. Into each sample, an agar nutrient dipstick was dipped into it for 20 minutes. The stick was then retrieved from the system and incubated in a warm oven for 24 hours. The population of the microorganisms was determined by comparing it with a calibrated chart provided by the manufacturer (Boots Micro – check company, Nottingham, UK).

All methods of analyses applied in this study are consistent to that of the Department of Petroleum Resources [34], American Public Health Association [35].

2.5 Treatment Systems and Process Flow

Fig. 2 shows the schematic diagram of the treatment system and process flow used in the study. The system is made of a receiving basin and a column of glass tube (50cm high and 9cm in diameter) packed with the bone char material to a level of 30cm. The column was packed by blocking both ends of the tube with glass wool. Raw groundwater sample was fed into a receiving basin from where varying concentrations of KMnO_4 was added and stirred properly to allow for good contact before being fed from the top. The flow under the influence of gravity at a flow rate of 2.5mL min^{-1} . Effluent outlet was at the bottom of the column.

2.6 Experimental Procedure

Bulked raw groundwater sample (1.5 liters) was divided into three equal portions (500ml) each. Each volume was treated with 50ml of standard solution of KMnO_4 at varying concentrations of 1.5mg/L, 2.0mg/L and 2.5mg/L. Each portion (KMnO_4 and raw groundwater) was agitated manually for 30 minutes to effect good groundwater – KMnO_4 contact. Each mixture was allowed to settle for 10 minutes. The resulting supernatant for each of the mixture was carefully decanted into a clean beaker and the resulting primary effluent was analysed for pH, temperature, dissolved oxygen, redox potential, iron oxidising bacteria (IOB) – *leptothrix discophora*, manganese and iron. Each of the primary effluent was gently poured down the column of animal bone char. The resulting secondary effluent was analysed for pH, temperature, dissolved oxygen, redox potential, iron oxidising bacteria (IOB) – *leptothrix discophora*, manganese and iron. Note that the bulked raw groundwater sample was also analysed for pH, temperature, dissolved oxygen, redox potential, iron oxidising bacteria (IOB) – *leptothrix discophora*, manganese and iron. The primary effluents (raw groundwater samples) were individually filtered through a fixed-bed of bone char. To prevent the problem of blocked column due to deposition of trapped flocs, three different columns of bone char were prepared for the study.

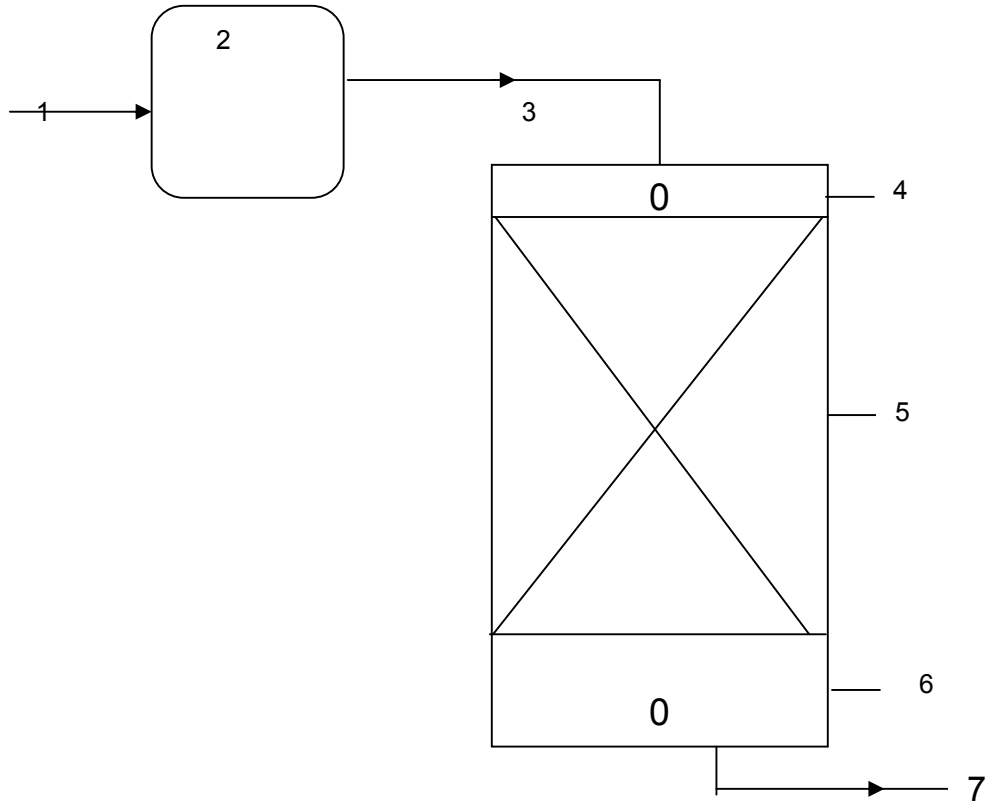
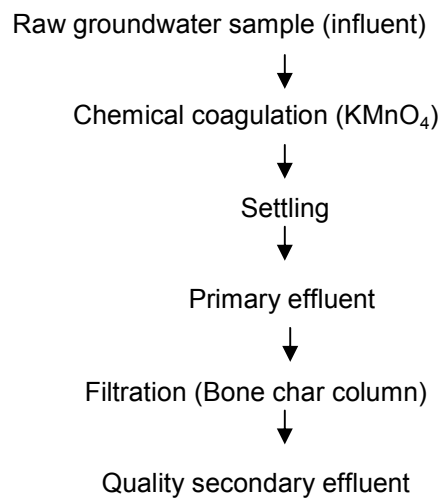


Fig. 2. Schematic diagram of the treatment process

Parts of the treatment system are: (1) Raw groundwater feed stream (2) Receiving basin (3) (3) primary effluent (4) Upper glass wool layer (5) Bone char packed layer (6) Lower glass wool layer (7) Effluent stream

The unit operations adopted in the treatment process are as follows:



3. RESULTS AND DISCUSSION

The characteristics of the groundwater samples are presented in Table 1. The pH values ranged from 5.9 to 6.3 indicating a slightly acidic medium. These values are not within the standard permissible limits for drinking water [36] but within suitable pH for the conversion of Fe^{2+} to Fe^{3+} [37]. The slight acidic pH may be linked with the characteristics of the Niger Delta region since movement of such salts from the surface of the soil to ground water might have occurred during seepage as ground water pollution can occur through seepage of pollutants and by migration of contaminants from the surface of the soil. This could be aided by the high infiltration and permeability of the soils (sandy loam soils) which implies that any contaminant on the surface has the potential to leach or move fast into the subsurface, which could lead to ground water contamination. Acidic environment with $\text{pH} < 6$ or alkaline environment with $\text{pH} > 8$ is more corrosive than an environment with pH in the range 6-8 [38].

Temperature of groundwater samples varied between 27.1°C and 27.5°C which is suitable for bacteria growth (optimal temperature for bacteria growth lies between 25°C and 30°C [39]).

Dissolved oxygen in all water samples ranges from 3.9mg/l to 4.2mg/l, indicating a partial aerated water sample and hence an environment that promotes growth of aerobic microorganisms. The level of oxygen in an environment plays an important role in corrosion process especially where oxygen reduction is generally the main cathodic reaction.

Redox potential (Eh) of all water samples lie within the range +107mV to +202mV. Spectrum of redox potential under which microbial life can be found ranges from -450mV to +850mV, where the negative side of the spectrum favours methanogenic bacteria, and the positive side corresponds to iron bacteria [40]. Thus, the positive redox potential values obtained for ground water samples indicate the presence of iron oxidizing bacteria.

The population of iron oxidising bacteria obtained in the ground water samples varies from 10^5 cfu/ml to 10^6 cfu/ml indicating adequate bacterial population for microbial corrosion activity. It has been suggested that Sulphate Reducing Bacteria (SRB) level of 10^4 cells/cm³ is a clear indication of possible corrosion problem, while a relative population of 10^6 cells/cm³ of microorganisms is a concern of potential corrosion problem in an environment [41].

Iron concentration in the ground water samples ranged from 3.02mg/l to 3.35mg/l. This element is in excess of the acceptable limits for drinking water. Iron exposure at high levels has been shown to result in vomiting, diarrhea, abdominal pain, seizures, shock, low blood glucose, liver damage, convulsions, coma and possibly death after 12 – 48 hours of ingesting toxic level of iron [42]. Death may also occur if children ingest sufficient iron to exceed the body's iron-binding capacity; the metal-binding proteins that make ionic iron available [43]. The nature and presence of iron in groundwater in the area indicates that the iron problem in the area is not migratory but of origin. It may be attributed to geological formation in the area as have been similarly observed [23].

The concentration of manganese (Mn) varies from 0.90mg/l to 1.06mg/l and is above limit of 0.02mg/l [44].

The above results indicate that ground water in the study area poses a threat to the survival of the inhabitants of the area who depend on this water source for their survival.

Analysis of treatment effluent obtained using varying concentrations of KMnO_4 (1.5mg/L, 2.0mg/L and 2.5mg/L) is presented in Table 3. Treatment process involving the use of 1.5 mg/L of KMnO_4 showed iron and manganese reduction from 3.28mg/L to 1.82mg/L and from 1.03mg/L to 0.97mg/L representing 44.51% and 5.85% reduction respectively. Iron oxidizing bacteria (IOB) was reduced from 10^6 cfu/ml to 10^4 cfu/ml reduction representing 99% reduction. Values of pH, temperature, dissolved oxygen (DO) and redox potential were also affected.

Treatment process involving the use of 2.0mg/L of KMnO_4 showed iron and manganese reduction from 3.28mg/L to 1.67mg/L and from 1.03mg/L to 0.81mg/L representing 49.09% and 21.36% reduction respectively. Iron oxidizing bacteria (IOB) was reduced from 10^6 cfu/ml to 10^2 cfu/ml reduction representing 99.99% reduction. Values of pH, temperature, dissolved oxygen (DO) and redox potential values were also affected.

Treatment process involving the use of 2.5mg/L of KMnO_4 showed iron and manganese reduction from 3.28mg/L to 0.97mg/L and from 1.03mg/L to 0.41mg/L representing 70.43% and 60.19% reduction respectively. Iron oxidizing bacteria (IOB) was reduced from 10^6 cfu/ml to 10^1 cfu/ml reduction representing 99.99% reduction. Values of pH, temperature, dissolved oxygen (DO) and redox potential values were also affected.

From Table 3, analysis of the treatment process using KMO_4 show that as the concentration of KMnO_4 increases the the oxidizing strenght increases and hence a higher percentage of reduction of iron and manganese. This finding is consistent with earlier reported study [44]. The reduction of iron oxidizing bacteria from 10^6 cfu/ml to 10^1 cfu/ml may be related to the biocidal efficacy of KMnO_4 against planktonic microorganisms as been similarly observed [45]. As the concentration of KMnO_4 increases the temperature of the reacting systems increases. Higher temperatures slightly enhance bactericidal action of potassium permanganate [44].

Analysis of treatment effluent obtained using a fixed bed of bone char is presented in Table 4. The treatment process showed iron and manganese reduction from 3.28mg/L to 2.93mg/L and from 1.03mg/L to 0.99mg/L representing 10.67% and 3.83% reduction. Iron oxidizing bacteria (IOB) was reduced from 10^6 cfu/ml to 10^5 cfu/ml reduction representing 9.0% reduction. Values of pH, temperature, dissolved oxygen (DO) and redox potential were also changed minimally.

Analysis of quality effluent obtained from the use of 2.5mg/L of KMnO_4 filtered through fixed-bed of bone char as depicted in Fig. 2 is presented in Table 5. The treatment process showed iron and manganese reduction from 3.28mg/L to nil and from 1.03mg/L to nil representing 100% reduction for both metals. Iron oxidizing bacteria (IOB) was reduced from 10^6 cfu/ml to 10^1 cfu/ml reduction representing 99.999% reduction. Values of pH, temperature, dissolved oxygen (DO) and redox potential were also affected.

In all treatment processes, it was generally observed that, the treatment process involving the use of 2.5mg/L dose of KMnO_4 filtered through a fixed bed of bone char achieved a corresponding reduction in the levels of all studied parameters. The fixed-bed of bone char can be linked to a natural filter where processes such as filtration, adsorption, biodegradation, ion-exchange and dispersion reduce contaminants to a great extent [46,47]. The application of KMnO_4 as an oxidizing agent in wastewater purification has been reported [44]. However, by fourth day of continuous operation of the treatment process using bone char, removal efficiency dropped. Major problem of the process was due to deposition of

trapped solids, which required back washing of the process column to regenerate it. Regeneration of the bone char column was done by back washing directly with tap water.

Table 1. Characterization of the raw groundwater samples (n=3)

Parameter/Units	BH 1	BH 2	BH 3	WHO [34]Standard for Drinking Water
pH	6.1	5.9	6.3	7.0-8.5
Temperature(°C)	27.3	27.1	27.5	25 – 30
DO (mg/l)	4.2	4.1	3.9	>5.0
Redox potential (mV)	+170	+202	+107	NA
IOB (cfu/ml)	10 ⁶	10 ⁵	10 ⁶	Nil
Iron (mg/l)	3.02	3.35	3.17	0.1
Manganese (mg/l)	0.93	1.06	0.90	200

Table 2. Chemical and physical characteristics of bone char [25]

Components/Characteristics	Content (%)
Ca ₃ (PO ₄) ₂	82.0 – 84.0
CaCO ₃	7.0 – 8.0
CaSO ₄	0.1-0.2
CaS	0.01-0.02
C	9.0-10.0
Apparent specific gravity	0.65-0.75
Effective diameter (mm)	0.4-1.0
Void ratio	52.0-58.0

Table 3. Quality of effluent obtained using varying concentrations of KMnO₄

Parameters	Characterisation of raw bulked groundwater sample	Varying concentrations of KMnO ₄		
		1.5mg/L	2.0mg/L	2.5mg/L
pH	6.0	6.8	7.4	8.3
Temperature(°C)	28.1	29.6	31.7	33.1
DO (mg/l)	4.1	3.7	3.3	3.1
Redox potential (mV)	+197	+205	+227	+276
IOB (cfu/ml)	10 ⁶	10 ⁴	10 ²	10 ¹
Iron (mg/l)	3.28	1.82	1.67	0.97
Manganese (mg/l)	1.03	0.97	0.81	0.41

Table 4. Quality of effluent obtained using a fixed bed of bone char

Parameters	Characterisation of raw bulked groundwater sample	Quality of Effluent
pH	6.0	6.3
Temperature(°C)	28.1	29.3
DO (mg/l)	4.1	3.9
Redox potential (mV)	+197	+203
IOB (cfu/ml)	10 ⁶	10 ⁵
Iron (mg/l)	3.28	2.93
Manganese (mg/l)	1.03	0.99

Comparison of results obtained in the treatment process involving the use of 2.5mg/L of KMnO₄ filtered through a fixed-bed of bone char showed a good compliance with World

Health Organisation [13] and Department of Petroleum Resources [34] (Table 5). This means that the final effluent obtained is safe for human consumption and poses no aesthetic nuisance.

Table 5. Effluent quality obtained from 2.5mg/L of KMnO_4 and a fixed bed of bone char

Parameters	Characterisation of raw bulked groundwater sample	Effluent Quality (Obtained with 2.5mg/L of KMnO_4 + a fixed bed of bone char)	Drinking water quality [13]
pH	6.0	6.7	6.5-8.0
Temperature ($^{\circ}\text{C}$)	28.1	29.6	25 - 30
DO (mg/l)	4.1	4.3	>5.0
Redox potential (mV)	+197	+271	NA
IOB (cfu/ml)	10^6	10^1	Nil
Iron (mg/l)	3.28	Nil	0.3
Manganese (mg/l)	1.03	Nil	0.2

4. Economics of the Treatment Process

The treatment process involving the use of KMnO_4 as an oxidizing agent and an adsorption column of animal bone char revealed that the adsorbent adsorbs iron and manganese to an appreciable extent, and therefore, can be fruitfully used for the treatment of iron containing water.

From the experimental set-up, it shows that show that 1kg of prepared animal bone char can treat 210 L of raw groundwater. It is therefore, reasonable to infer that the prepared adsorbent can be fruitfully used as an alternative adsorbent for treating iron rich containing groundwater.

Commercial activated carbons (generally used for effluent treatment) cost \approx US\$ 2000 tonnes⁻¹ in Nigeria. The waste material used in the present study is generally available at a very cheap rate \approx US\$ 1- 3 tonnes⁻¹. The treatment process would cost approximately \approx US\$ 10-15 tonnes⁻¹ by adding all expenses (transportation, chemicals (KMnO_4), electrical energy, etc.). Since the cost of final adsorbent prepared from waste animal bone is 60 times less than the cost of activated carbons used in conventional treatment, it is reasonable to conclude that animal bone char can be fruitfully used as low-cost adsorbents for the treatment of raw groundwater.

5. CONCLUSION

This study has demonstrated that groundwater sample with elevated levels of iron when subjected to 2.5mg/L of KMnO_4 and filtered through a fixed bed of bone char have the potential to reduced such water sample to acceptable limits. The treatment technology was found to be environmentally friendly and highly efficient and potentially cost-effective.

COMPETING INTERESTS

Author has declared that no competing interests exist.

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