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# Effectiveness of an inorganic coagulation - disinfection - adsorbent prepared product for the removal of heavy metals on boreholes water in Onicha town of Ebonyi State, Nigeria.

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***Abstract:*** *The present work has formulated an effective inorganic coagulation-disinfection-adsorbent using iron (III) sulphate, calcium hypochlorite and ash prepared from locally available raw materials of scrap metal from Abakaliki mechanic village, carbide sludge derived from calcium carbide in oxy-acetylene welding shops and unripe banana peels respectively. The effectiveness of the formulation was investigated on five borehole water samples used for drinking in Onicha towns of Ebonyi State, Nigeria and compared with World Health Organization (WHO) guideline limit . The result showed that heavy metals (Cd, Cr, Pb, Cu, Mn, Zn) were reduced after treatment of the water with the product. This work is to give information on the nature of the boreholes water in Ebonyi State and to provide solution on how to remove heavy metals from heavy metal contaminant boreholes.*

***Keywords:*** *coagulation-disinfection-adsorbent, boreholes water, heavy metals*

## I. Introduction

Access to potable water is a basic human right that is supposed to be enjoyed every day. However, this right eludes millions of people all over the world [1]. The World Health Organization (WHO) estimates that 1.1 billion lack access to clean drinking water. More than half of these proportions stay in the developing countries of Africa such as Nigeria which result in 2.2 million deaths each year arising from drinking unclean water. The most affected are children of 5 years and below. Prior to this time, drinking unclean water meant high risk to diarrhea disease and other water borne diseases caused by pathogenic microorganisms.

Recently, bacteria and parasites in the drinking water of the developing countries are no longer the only problems, but issues of heavy metals pollution coming through industrial mining and sewage dumps are now adding to the water problems. Exposure to toxic heavy metals such as mercury, lead, arsenic, cadmium can cause neurological problems, chronic diseases such as cancer and inhibit development in children. [2] published an article titled “from Guineaworm’s scourge to metal toxicity in waters in Ebonyi State”. The publication revealed that contaminants levels of toxic metals in Ebonyi State water exceeded by far the recommended limit of the World Health Organization for drinking water qualities. Study carried out by Obasi and his colleagues in (2015) on heavy metals in borehole waters in Abakaliki revealed toxic metal levels to be Cd (0.11-0.036 $mgL^{-1}$), Hg (0.069-0.70 $mgL^{-1}$); Pb (0.4-0.8)$mgL^{-1}$), against [3] guideline standard of 0.003$mgL^{-1}$ for Cd, 0.01 for Pb and 0.01$mgL^{-1}$ for As. Survey of different water sources used as potable water in Ebonyi State by [3] in 2006 revealed that 42% of the populace depends on borehole, 9% on contact springs, 16% on pipe borne water, while 33% source their water needs from doubtful sources such as shallow wells, dams, rivers, rain water and water vendors such as sachet waters.

The quality of borehole water in Ebonyi State limits its use. Characteristic include high levels of heavy metal content, salty taste, hardness, turbidity, odour, etc [4]. These problems may be attributed to the geology and hydrogeology of the area which include the presence of limestone, gupsum and dolomite at Abakaliki which may introduce calcium and magnesium salts. Other mineral deposits present at high levels in aquifers in the state include Pb, Zn, As, Mn, Cu, Cr, P and $F^-$ (Ministry of Commerce and Industry, Ebonyi, 2001). [5] reported that the quality and composition of borehole waters in Ebonyi State are odourless, colourless, but salty taste. Notwithstanding, careful observation of some borehole water samples showed that water sourced from some boreholes often have brownish thin films on the surface after about 30 mins.

Studies have demonstrated that home water treatment and safe storage interventions can improve water quality in developing countries such as Nigeria [6]; [7]. Among the five options recognized by the World Health Organization [8], the most widely used is the flocculation-disinfection technology developed by the Procter and Gamble Company called PuR water purifier in 2001 [9], [10]. This is because it incorporates the multiple treatment approach of particles removal and disinfection. Laboratory tests and field trials showed that PuR removes vast majority of bacteria, viruses and protozoa even in high turbid water [11]. PuR reduces diarrhea from 90 to less than 16%, remove heavy metals and inactivate microbes. Equally numerous technologies developed to specifically remove heavy metals such as silica, alumina, activated carbon and resins are successful and effective, but only in developed countries. This is because the cost of manufacturing and distribution of these products in developing countries are expensive and almost not feasible. In Brazil, banana peels removed Cu and Pb in water from Paranhas River. Banana peels contain anions which can bind the toxic metals and remove them out of the water [12].

This study prepared an inorganic coagulation – disinfection – adsorbent product using iron (III) sulphate prepared from scrap metal, calcium hypochlorite prepared from carbide sludge and ash from unripe banana peels. Iron (III) sulphate was used as coagulant, calcium hypochlorite as disinfectant and ash as an adsorbent. The effectiveness of the product in removing heavy metals was investigated on five borehole water samples used as sources of drinking water by Onicha community in Ebonyi State, Nigeria between November, 2013 – January, 2014 and May – July, 2014.

## II. Materials And Method

All reagents used were of analytical grade (Merck products, Germany) and were used without further purifications. Notwithstanding, dilutions were made where necessary.

**Preparation of $Fe_2(SO_4)_3$, $Ca(OCl)_2$ and ash from waste (raw materials)**:

**$Fe_2(SO_4)_3$:** Extractive method according to CR Scientific [13] was used in preparing iron (III) sulphate. Granulated and degreased scrap metal (100.0g) were weighed into 250cm$^3$ glass beaker and enough 35% sulphuric acid added into the beaker which dissolved the scrap metal.

$$Fe + H_2SO_4 \longrightarrow FeSO_4 + H_2$$

The solution was filtered after 2h and the filtrate concentrated by evaporation for 30 mins using water bath at 80$^o$C, then cooled to room temperature and allowed to stand for 24h to form enough green crystals of $FeSO_4.7H_2O$. The crystals were removed by decanting the liquid and transferred to a desiccator having calcium chloride pellets to dry the crystals.

Accurately weighed 30.0g of $FeSO_4.7H_2O$ was put into 250cm$^3$ beaker and 35% $H_2SO_4$ and 30% $H_2O_2$ added in the ratio 2:1:1 of $FeSO_4 : H_2SO_4 : H_2O_2$ and heated on a water bath in which reddish brown crystals was formed and after 2h, the liquid was decanted, while the crystals were washed with distilled de-ionized water and dried to constant weight and weighed, tested according to Ababio, (2010) method and found to iron (III) sulphate.

$$2FeSO_4 + H_2SO_4 + H_2O_2 \longrightarrow Fe_2(SO_4)_3 + 2H_2O$$

The **$Ca(OCl)_2$**: Calcium hypochlorite was according to the methods of the [14] [15]. Collected carbide sludge from welder's shop in Ezzamgbo Junction was sun dried for 7 days, homogenized with lab mortar and sieved. The sieved sample (1.0 Kg) was added to 1.0 L of water and allowed for 24 h. After 24 h, the mixture was filtered and the filtrate was dried to a constant weight in an oven at 105 $\pm$ 3 $^o$C which was the slaked lime, ($Ca(OH)_2$).

$$CaC_2 + 2H_2O \longrightarrow C_2H_2 + Ca(OH)_2.$$

Two stages chlorination process was used. Solid slaked lime sample (57.0g) and 112.0mL suspension obtained from the prepared slake lime were weighed into 250 cm$^3$ conical flask with magnetic stirrer. $KMnO_4$ (40.0 g) was weighed into another conical flask having thistle funnel through which conc. HCl was passed into the flask. The flask was connected to two aspirator bottles containing water and $H_2SO_4$ respectively to the flask having the $Ca(OH)_2$ suspension. $Cl_2$ was passed into flask as shown in Fig. 1 at a temperature of 50 $\pm$ 5 $^o$C and the product obtained was filtered using Buchner filter in a vaccum.

$$2KMnO_4 + 16HCl \longrightarrow 2MnCl_2 + 2KCl + 8H_2O + 5Cl_2$$

$$2Ca(OH)_2 + 2Cl_2 \longrightarrow Ca(OCl)_2 + CaCl_2 + 2H_2O.$$

Then 27.0g of the residue, 28.5mL of distilled water and 2.1g of NaOH were added to 250cm$^3$ conical flask with magnetic stirrer and the temperature adjusted to 35 $\pm$ 5$^o$C and chlorine immersed for 3h. The pH of the suspension at the end of reaction was 9.3 and the flask removed from the reactor (thermostatically controlled bath) and the suspension filtered through Buckner filter. The solid (residue) was washed with 10.0cm$^3$ of distilled water and dried at 65$^o$C and the active chlorine content was 59.6%.

**Preparation of Ash from Banana (*Musa sapientum*) Peel Waste**

The methods of [16] [17] were followed. Unripe banana bunch bought at Eke market, Ezzamgbo was washed with distilled water and peeled. The peels were sun dried for a week and oven dried for 2 hrs at 200 ± 5$^o$C. Weighed 150.0 g of the peels were ashed using zinc sheet and then allowed to cool for 3hrs and weighed.

**Reagents for the Flocculent–Disinfectant Formulation**

Iron (III) sulphate (25.0g) was dissolved in 250cm$^3$ volumetric flask and made to the mark with distilled de-ionized water.

Calcium hypochlorite (1.0g) was equally dissolved in 250cm$^3$ volumetric flask and made to the mark with distilled de-ionized water.

Banana peels ash was also prepared by dissolving 5.0g of the ash in 250 $cm^3$ and made to the mark with distilled de-ionized water, covered and allowed to stand for 24h, filtered and filtrate used for the formulation of the product. All the reagents served as stock solutions in the formulation.

**Application of the Metal-Based Coagulation – Disinfection - Adsorbent**

The formulated product was applied to the water sample by adding the content to the 1000.0 $cm^3$ of water in the containing vessels, stirred for 1 min, allowed to settle for 30 mins and filtered with white cloth. The treated water appears clearer and cleaner (CDC, 2001).

**The efficacy of the prepared product**

The efficacy of the prepared product was tested on five heavy metals contaminated borehole water in Onicha town, Onicha Local Government of Ebonyi State for the removal of heavy metals. The metals analyses were carried out using atomic absorption spectroscopy (AAS) (Buck Scientific, 205), while flame photometer (Elmer Perkin - 52) was used for the determination of K and Na.

**Statistical Analysis Using One-Way ANOVA**

Summary of the results were presented in mean and standard deviation. Statistical Analysis was carried out using statistical package for social sciences (SPSS) software for Microsoft excel.
The results obtained were subjected to one-way analysis of variance (ANOVA) using Student Newman Keuls (S-N-K) post hoc test. The results were tested at $p < 0.05$ at 95% confidence level to determine significance difference of variations between multiple variables. Results at $P < 0.05$ were considered significant.

## III. Results And Discussion

Tables 1 presented the results of mean metal concentrations of five borehole water samples in Onicha town from November, 2013 to January, 2014 (dry season) compared with WHO standard, 2011. The Table 1 revealed that cadmium, chromium, manganese, and iron were high in all the five borehole samples in Onicha above WHO's guideline limit from November, 2013 to January, 2014 (dry season). Lead was also high in Egunkwor and Ubewa water samples above WHO's recommended limit of $0.01mgL^{-1}$ before treatment. This is in conformity with the finds of [18] [19] that borehole waters in Ebonyi State contents excess toxic metals. The presence of these toxic metals in excess indicates danger and drinking such boreholes without treatment may suffer liver and kidney damages, asthma and permanent disability [20]; [21].

After treatment (AT) of the water samples with the prepared product, all water samples both essential metals like copper, sodium and zinc as well as the toxic metals such as cadmium, manganese, lead, etc were reduced to the WHO's recommended limits, showing the effectiveness of the prepared product in removing metals from metal contaminated water. Potassium was not reduced in the treated water and could be due to ionic effect [22] or high level of potassium in the banana peels ash [3].

Although cadmium was reduced after treatment, it was still higher in samples from Egunkwor ($0.01\pm0.08mgL^{-1}$), Amaodidia ($0.005\pm0.00mgL^{-1}$) and Amakporo ($0.004\pm0.00mgL^{-1}$) above WHO guideline limit of $0.003mgL^{-1}$. This could be as result of high cadmium in the borehole waters.

Statistical analysis showed no significant difference for the metals before treatment and after treatment, but showed significant difference between the treated and untreated water samples at $P < 0.05$. This is an indication of the efficacy of the prepared product in removing heavy metals from heavy metal contaminated water.

**Table 1:** Metal Concentrations of Onicha Borehole Water Samples from Nov.2013 to Jan. 2014

| Locations | Egunkwo | | Ubewa | | Ibechima | | Amaodidia | | Amakporo | | WHO, 2011 |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Metals ($mgL^{-1}$) | BT | AT | BT | AT | BT | AT | BT | AT | BT | AT | - |
| Aluminum | 0.02±0.00 | 0.004±0.00 | 0.03±0.02 | 0.003±0.07 | 0.04±0.07 | 0.01±0.02 | 0.01±0.04 | ND | 0.05±0.00 | 0.008±0.04 | 0.02 |
| Calcium | 44.9±0.21 | 20.4±0.20 | 23.2±0.12 | 11.6±0.08 | 30.4±0.34 | 17.2±0.56 | 25.2±0.19 | 10.0±0.11 | 30.4±0.56 | 12.0±0.11 | 75 |
| Cadmium | 0.11±0.11* | 0.01±0.08 | 0.08±0.08* | 0.003±0.17 | 0.08±0.21* | 0.003±0.06 | 0.13±0.09* | 0.005±0.00* | 0.09±0.22* | 0.004±0.00* | 0.003 |
| Chromium | 0.03±0.08 | 0.01±0.00 | 0.03±0.09 | 0.01±0.14 | 0.04±0.11 | 0.014±0.12 | 0.02±0.23 | ND | 0.02±0.04 | 0.001±0.00 | 0.05 |
| Copper | 0.73±0.15 | 0.20±0.04 | 0.08±0.16 | 0.006±0.08 | 0.03±0.00 | 0.002±0.20 | 0.15±0.12 | 0.35±0.21 | 3.02±0.02* | 0.43±0.11 | 1.0-1.5 |
| Magnesium | 14.9±0.07 | 7.23±0.09 | 7.0±0.28 | 2.61±0.12 | 11.04±0.21 | 2.01±0.12 | 6.02±0.07 | 1.91±0.09 | 5.02±0.21 | 2.41±0.18 | 50 |
| Manganese | 1.6± 0.17* | 0.03±0.11 | 0.08±0.21* | 0.01±0.09 | 0.19±0.28* | 0.024±0.34 | 0.87±0.12* | 0.02±0.17 | 0.06±0.11* | 0.001±0.04 | 0.05 |
| Sodium | 5.03±0.12 | 2.03±0.04 | 3.05±0.04 | 0.71±0.16 | 2.05±0.12 | 0.75±0.12 | 3.51±0.35 | 0.82±0.07 | 2.90±0.17 | 0.61±0.02 | 100 |
| Potassium | 3.27± 0.23 | 3.51±0.11 | 3.87±0.09 | 4.12±0.12 | 1.95±0.56 | 2.14±0.08 | 5.35±0.08 | 5.67±0.04 | 2.47±0.04 | 2.71±0.08 | - |
| Zinc | 4.50±0.11 | 0.56±0.21 | 3.08±0.10 | 0.41±0.23 | 5.90±0.12 | 1.07±0.12 | 4.10±0.12 | 0.55±0.08 | 0.45±0.16 | 0.56±0.09 | 5.0 |
| Iron | 1.00±0.08* | 0.02±0.31 | 0.70±0.18* | 0.22±0.34 | 0.60±0.10* | 0.01±0.27 | 0.30±0.46 | 0.05±0.11 | 0.61±0.07* | 0.02±0.00 | 0.3 |
| Lead | 0.07±0.00* | ND | 0.06±.0.1* | 0.003±0.08 | ND | ND | 0.02±0.12* | ND | 0.02±0.00* | 0.001±0.00 | 0.01 |

*BT = before treatment with product, AT = after treatment with the product. ND=not detected*

**Table 2:** Metal Concentrations of Onicha Borehole Water Samples from May to July 2014.

| Locations | Egunkwo | | Ubewa | | Ibechima | | Amaodidia | | Amakporo | | WHO ,2011 |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Metal($mgL^{-1}$) | BT | AT | BT | AT | BT | AT | BT | AT | BT | AT | - |
| Aluminum | 0.01±0.00 | ND | 0.02±0.02 | 0.005±0.07 | 0.03±0.11* | 0.007±0.04 | 0.01±0.00 | ND | 0.04±0.02* | 0.008±0.02 | 0.02 |
| Calcium | 42.9±0.64 | 20.0±0.21 | 20.8±0.11 | 11.2±0.0.11 | 29.6±0.27 | 16.8±0.22 | 24.4+0.09 | 9.60±0.11 | 28.0±0.42 | 11.6±0.09 | 75 |
| Cadmium | 0.09±0.02* | 0.003±0.02 | 0.07±0.07* | 0.001±0.09 | 0.07±0.17* | 0.001±0.00 | 0.12±0.02* | 0.01±0.0* | 0.03±0.04* | 0.005±0.00* | 0.003 |
| Chromium | 0.02±0.00 | 0.001±0.04 | 0.022±0.00 | 0.003±0.00 | 0.03±0.02 | 0.009±0.07 | 0.02±0.15 | ND | 0.01±0.09 | ND | 0.05 |
| Copper | 0.70±0.09 | 0.15±0.07 | 0.070±.09 | 0.009±0.00 | 0.03±0.09 | 0.06±0.00 | 0.004±0.04 | 0.02±0.01 | 0.02±0.00 | ND | 1.5 |
| Magnesium | 14.5±0.12 | 7.23±0.24 | 7.03±0.04 | 2.61±0.12 | 11.04±0.14 | 2.11±0.24 | 6.31±0.09 | 3.82±0.25 | 5.62±0.12 | 2.31±0,21 | 75 |
| Manganese | 0.60±0.10* | 0.04±0.08 | 0.07±0.21* | ND | 0.12±0.12* | 0.02±0.11 | 0.79±0.21* | 0.05±0.00 | 0.06±0.17* | 0.002±0.00 | 0.05 |
| Potassium | 3.20±0.11 | 3.45±0.02 | 3.87±0.17 | 4.09±0.21 | 1.93±0.06 | 2.11+0.23 | 5.35±0.02 | 5.62±0.12 | 2.43±0.09 | 2.68±0.17 | - |
| Sodium | 4.95±0.16 | 2.00±0.06 | 2.89±0.09 | 0.06±0.10 | 1.98±0.09 | 0.61±0.09 | 3.50±0.12 | 0.73±0.10 | 2.43±0.01 | 0.56±0.08 | 100 |
| Zinc | 4.38±0.32 | 0.51±0.04 | 2.97±0.08 | 0.35±0.21 | 5.90±0.011 | 1.04±0.20 | 4.10±0.17 | 0.53±0.21 | 0.45±0.08 | 0.55±0.24 | 5.0 |
| Lead | 0.02±0.12* | ND | 0.05±0.06* | 0.003±0.01 | ND | ND | 0.01±0.00 | ND | 0.03+0.04* | ND | 0.01 |
| Iron | 0.97±0.07 | 0.20±0.17 | 0.67±0.09 | 0.02±0.04 | 0.60±0.18 | 0.01±0.12 | 0.28±0.08 | ND | 0.45±0.11 | 0.02±0.00 | 0.03 |

*BT = before treatment with product, AT = after treatment with the product. ND=not detected*

Table 2 gives information about the mean concentrations of heavy metals and non- heavy metals in five borehole water samples in Onicha town before and after treatment with the coagulation – disinfection – adsorbent prepared product between May to July, 2014 (rainy season) compared with WHO's guideline limit, 2011. The Table showed that cadmium, manganese, and iron were high in all the borehole samples above WHO's guideline limit as indicated by out outseick. Lead was also high in Egunkwor and Ubewa water samples above WHO's recommended limit before treatment. After treatment with the prepared product, all the metals both essential and toxic metals were reduced in the treated water samples except potassium. However, cadmium although reduced after treatment, yet was still slightly higher in samples from Amaodidia (0.01+0.00 $mgL^{-1}$) and Amakporo (0.005±0.00$mgL^{-1}$) above WHO guideline of 0.003$mgL^{-1}$.

This is in agreement with [5] [6] which said that banana peels ash contents reasonable quantity of potassium. From the results, the prepared product is effective in removing heavy metals out of heavy metal contaminated water [12]; [13]. The removal of sodium increases the ratio of potassium to sodium. This is an added advantage because increase in potassium to sodium ratio in the body fluid reduces high blood pressure and muscle cramps [9].

Statistical analysis revealed significant difference between the treated and untreated water samples at $P < 0.05$. This is an indication that the prepared product is effective in removing heavy metals and essential metals from water. There was also no statistical difference between the metal concentrations for periods between November, 2013 to January, 2014 (dry season) and May to July, 2014 (rainy season) could be due to aquifers in Ebonyi State being secondary aquifers and not primary.

## IV. Conclusion

All the borehole water samples tested had heavy metals above WHO recommended limit, 2011. The prepared coagulation – disinfection – adsorbent was effective in removing not only heavy metals, but also all the metals except potassium.

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