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ANALYSIS AND TREATMENT OF PRODUCED WATER (IGBO-ETCHE) USING NATURAL BIOCOAGULANT FROM *Inga edulis*

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ABSTRACT

Produced water from Igbo-Etche a community in Rivers State (Niger Delta), Nigeria was analyzed and treated with Inga edulis a potential biocoagulant. It was observed that pH value was within the permissible limits of National Environmental Standard and Regulation Enforcement Agency (NESREA) limit of 6.50-9.50. Turbidity value of (49NTU); concentrations for chloride (21,872mg/l), polycyclic aromatics hydrocarbons (90.79 mg/l), oil and grease (17,742 mg/l) were reduced to 2NTU, 6351.7 mg/l, 13.72 mg/l and 2,884 mg/l respectively on treatment with Inga edulis. The biocoagulant had no effect on conductivity and chromium. However, there was an increase in the concentrations of total carbon (TC), total inorganic carbon (TIC), total organic carbon (TOC), biological oxygen demand (BOD) and chemical oxygen demand (COD) after treatment. The concentrations of iron, cadmium, chromium, copper and manganese in the untreated sample were below NESREA/WHO permissible limit. The high concentrations of nickel, zinc and lead in the untreated produce water sample were reduced after treatment with the biocoagulant. The 1.0g/63µg coagulant treatment gave higher reduction than 2.5g/63µg in most parameters.

Keywords: Biocoagulants, polycyclic aromatic hydrocarbon, mutagenic, crude oil, eco-system, biodegradable and teratogenic

INTRODUCTION

The production of crude oil and gas hydrocarbon results in a by-product called produced water. Produced water is basically a mixture of formation water and injected water but also contains smaller quantities of dissolved organics (included hydrocarbons), traces of heavy metals, dissolved minerals, suspended oil (non-polar), solids (sand, silt) and production chemicals (Veil *et. al.*, 2005, Yang and Nel**,** 2006, Grigson *et. al.* 2010). These dissolved hydrocarbons are found naturally in formation water and can be both toxic and bio-accumulative. The water-soluble components found in produced water are mainly BTEX (benzene, toluene, ethyl benzene and xylene), polycyclic aromatic hydrocarbons (PAHs) and alkylphenols, and together with heavy metals are considered harmful contaminants in produced water. The concentrations of these contaminants are continually changed because of injection of seawater, reinjection of produced water, reservoir stimulation, bacterial activity, introduction of production chemicals, treatment chemicals and more (Cline 1998).

The long-term effects of such contaminants on the environment are not fully documented and understood. Results have shown that fish exposed to alkyl phenols have disturbances in both organs and fertility (Ramirez, 1993). Also, trace elements, hydrocarbons and radionuclides accumulate in the sediments and food chain; and they present a source of exposure to aquatic birds (Rattner *et. al.* 1995, Grau *et. al.* 1977).

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These contaminants adversely affect humans because PAHs such as anthracene, phenanthrene, benzo(a)pyrene and benzo(a)anthracene have been a major health concern because of their toxicity (Fetzer, 2000). Some of these and other PAHs have been identified as carcinogenic, mutagenic and teratogenic (Luch, 2005 and Halek *et. al.* 2008). These results are serious and require further investigations. The petroleum industry, governments and scientists have agreed that more attention be placed on dissolved organic components, heavy metals and production chemicals. Similarly, oil in water content shall be as low as possible and industries should make use of best available technology (BAT).

There is the need for constant monitoring of various parameters to make sure that accepted standards are adhered to and that samples are treated to meet the required standard. Produced water can also be treated like other wastewaters using these treatment methods but these are quite expensive and require skilled staff (Bromley *et. al.* 2002; Galambos *et. al.* 2004; Amuda *et. al.* 2006; Wang *et. al.* 2007).

Current use of alum in water treatment has been associated with health hazards in human such as the Alzheimer's disease. Raising the competitiveness of plant based bio coagulants and promoting its large scale use in the water treatment industry may be a positive step towards improving human health. Environmental benefits: One of the major issues in using alum for water treatment is the generation of polluting sludge at a significant cost to the environment. The environmental benefits no doubt are also linked to a need for regulatory policy changes from the government. Biocoagulant are biodegradable, harmless and lack secondary pollution as such have received much wider attention and investigation to date (Sanayei *et. al.* 2010). Biocoagulant such as *Moringa oleifera*, *Strychnos potatorum* and *Bridelia ferruginea* contain natural polyelectrolytes which can be used as coagulants to clarify turbid waters (Nwaugo *et. al.* 2006, Amuda *et. al.* 2006, Kolawole *et. al.* 2007).

This paper reports the use of *Inga edulis* (Obuzor and Ejimozor, 2010) leaf extract for the treatment of produced water from Igbo-Etche a community in Rivers State (Niger Delta), Nigeria. This will be achieved by studying the effect of Inga edulis on pH, turbidity, conductivity, COD, BOD, polycyclic aromatic hydrocarbon (PAH), oil and grease and metal ion content of produce water. The resultant sediment is hoped to be both bio-degradable and eco – friendly.

National Environmental Standard and Regulation Enforcement Agency (NESREA) is the new regulatory body set by the Federal Government of Nigeria that has replaced the functions of Federal Environmental Protection Agency (FEPA).

MATERIALS AND METHOD

EXPERIMENTAL

Water Collection

The produced water used in this work was obtained from the Christmas tree ready for discharge at Egbeda II flow stations in Ikwerre Local Government Area but the well which generates the produced water is in Igbo-Etche in Etche Local Government Area, Rivers State, Nigeria. The produced water was collected using sterile plastic container. This was taken to the laboratories within four hours of collection for various analyses.

The *Inga edulis* leaves were obtained from an *Inga edulis* tree at the Rivers State University of Science and Technology Campus, Port-Harcourt, Rivers State.

PREPARATION OF THE LEAF EXTRACT

The leaves were air-dried until a constant weight was obtained. The dried leaves were then pulverized using a laboratory mill, the powder obtained was sieved using 63µm mesh sieve and

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stored; from which appropriate amounts were taken for subsequent experiment. One hundred and fifty nine grams of the powdered leaves sample was suspended in solvent combination of water and ethanol (1:2) at room temperature for 48 hrs with constant stirring. This was allowed to settle, decanted and filtered using sterile Whatman paper (No. 1). The filtrate was concentrated to dryness at 45 ^{O}C in a rotary evaporator. The residue obtained served as leaf extract (Natural biocoagulant).

METAL ION ANALYSIS

1.0g of grinded lnga-edulis (10ml produce water sample) was digested using mixed acid method (10ml HNO_3 and 5ml 52% perchloric acid) and analyzed for the desired metal ions by Atomic Absorption Spectrometry while phosphorus was determined by Ascorbic acid method (Lenore *et. al*. 1999).

DETERMINATION OF PAHS, OIL AND GREASE, TURBIDITY AND pH.

1.0g and 2.5g of the coagulant were weighed and each dissolved in the produced water samples [80ml]. The samples were agitated using Stuart flash shaker for 24hrs to ensure coagulation. The coagulated samples were then allowed to settle overnight and the PAHS values determined using gas chromatograph HP 5890 Series II, oil and grease values were determined using spectrophotometer HACH DR 2400. A HACH 2100N Turbidimeter was used to obtain turbidity after calibration to 0.1 nephelometric turbidity unit (NTU), NTU, 20NTU, 200NTU, 1000NTU and 4000NTU. An Orion digital pH / millivolt meter 611 was used to measure the pH after calibration with standard pH tablets of pH 4, 7, and 9.2. A Thermo Orion was used to obtain conductivity after calibrating with 0.001M KCl. Biological Oxygen Demand (BOD) and Chemical Oxygen Demand (COD) were analyzed by standard methods (Lenore *et. al*. 1999).

RESULTS AND DISCUSSION

Analysis of *Inga edulis* leaf extract gave partial electrolytic content of the natural biocoagulant as reported in Table 1. This biocoagulant is safe and its chemical analysis compares favourably to *Moringa oleifera* which is an edible leaf (Nwaugo *et. al.* 2006). The concentration of polycyclic aromatic hydrocarbons (PAHs) of Igbo-Etche produced water is 90.79mg/l as presented in Table 2. This value is well above National Environmental Standard and Regulation Enforcement Agency (NESREA) permissible limit of 7mg/l. A total of fourteen (PAHs) were identified with six of them (Acenaphthyene, Acenaphthene, Fluorene, Phenanthrene, Anthracene and Fluoranthene) well above the total permissible limit of 7mg/l. These (PAHs) are low molecular weight PAHs (LM-PAHs), those containing two to three rings constitute 79% (71.77mg/l) of the total PAHs while the high molecular weight (HM-PAHs) (benzo [a] anthracene, chrysene, benzo [b]fluoranthracene, benzo[a]pyrene, indeno [1,2,3] pyrene, dibenz [a,h] anthracene and indeno[1,2,3-c,d]pyrene) containing four to six rings are all less than 7mg/l, make up 19% (17.33mg/l) of the total concentration. LM-PAHs are predominant species (Table 2); these are known carcinogens and they react with other pollutants to form more toxic derivatives (Ho *et. al*. 2002) while the mutagenic and teratogenic species are the HM-PAHs (Lee *et. al.* 2002). On treatment with *Inga edulis* (PAHs) had 85% (13.72mg/l) reduction using 1.0g/63µg after 24hr of treatment and a 21% (71.79mg/l) reduction with 2.5g/63µg after 24hr of treatment Table 2. These values (13.72 and 71.79mg/l) are above NESREA permissible limit of 7mg/l yet lower than the initial PAHs concentrations that were being discharged.

The physicochemical parameters are presented in Table 3 and the pH values were all within the permissible limits of NESREA. Turbidity of the untreated sample that was

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49NTU was reduced to 2 NTU (96% reduction) after 24hr of treatment with 1.0g/63μg. This is below the permissible limit of 5 NTU while treatment with 2.5g/63μg coagulant gave reduction of 78% (11 NTU). This reduction is better than that obtained by using *Moringa oleifera* which gave 80% reduction (Nwaugo *et. al.* 2006). Conductivity values were below permissible limit. Original concentration of oil and grease concentration was 17,742mg/l. A reduction of 84% (2,884mg/l) at 1.0g/63μg and 29% (12,586mg/l) at 2.5g/63μg were obtained after 24hr treatment with the biocoagulant. This reduction is still above NESREA

Permissible limit of 0.01mg/l however, if this treatment could be done as a preliminary treatment or in combination with another; then more of the oil and grease could be removed. *Ortho*-phosphate (0.18mg/l) was reduced to 0.02mg/l on treatment with 2.5g/63μg after 24hr. This value is below NESREA permissible limit of 5.5mg/l (Table 3). Treatment of the produced water with 1.0g/63μg after 24hr gave an increase in *ortho*-phosphate indicating that 2.5/63μg is more effective in reducing o*rtho*-phosphate concentration. There was a reduction of the chloride content although not close to the limit. Biological oxygen demand (BOD) and chemical oxygen demand (COD) concentration were higher than permissible limits. There was a general increase in the concentrations of total carbon, total inorganic carbon and total organic carbon after the sample was treated with the biocoagulant (*Inga edulis* leaf extract). This increase in BOD and COD was also observed by Kolawole *et. al.* 2007 when wastewater was treated with *Bridelia ferruginea benth bark* extract. Increase in these parameters is probably caused by the bioaccumulation of the degrading PAHs.

The concentrations of iron, zinc, cadmium, chromium, copper and manganese in the untreated sample were below NESREA permissible limit (Table 3) but after treatment the concentrations zinc, copper, nickel and manganese increased above permissible limits. There is a probability that the biocoagulant (Table 1) had impacted on the produced water sample.

Table 1. Determination of metallic content of Inga edulis leaf (mg/l)

Parameter	Fe	Zn	Cu	Mn	Ca	K	Mg	Na	P
Values	4.57	0.448	0.285	1.124	76.10	91.24	12.99	5.42	1.345×10^{-3}

Table 2: Polycyclic aromatic hydrocarbon concentration of Igbo-Etche petroleum produced water

PAHS (mg/l)	Conc. before treatment	Conc. after treatment 1g/63μm	Conc. after treatment 2.5g/63μm
Naphthalene	1.690	0.1603	6.607
Acenaphthyene	8.768	0.11236	3.175
Acenaphthene	9.616	0.6957	9.144
Fluorene	9.622	1.395	11.99
Phenanthrene	8.0646	1.410	5.421
Anthracene	17.81	0.3406	9.092
Fluoranthene	17.89	2.774	11.75
Benzo[a]anthracene	4.556	1.189	4.557
Chrysene	2.469	0.3714	5.013
Benzo[b]fluoranthene	1.693	0.2643	1.009
Benzo[a]pyrene	3.166	0.2157	0.6335
Indeno[1,2,3]pyrene	0.5896	0.5262	0.79076
Dibenz[a,h]anthracene	0.5655	1.834	0.6538
Indeno[1,2,3-cd]pyrene	4.293	2.431	2.100
Total concentration	90.79	13.72	71.94
Percent reduction		84.88	20.76

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Table 3. Physicochemical Properties of Igbo-Etche Produced Water.

Parameters	Untreated sample	Treated 1.0g/63µg for 24hr	Treated 2.5g/63µg for 24hr	Maximum Permissible Limit (WHO)
pH	8.30	8.5	8.6	6.50-9.50
Turbidity[NTU]	49	2.0	11	10
Conductivity (µs/cm)	21	25.4	22.6	1,200
Oil and grease (mg/l)	17,742	2,884	12,586	0.01
PAH (mg/l)	90.79	13.72	71.94	7
M-Alkalinity (mg/l)	2,030	2,060	2,111.5	100
Chloride (mg/l)	21,871.55	6,575.3	6,351.7	250
Ortho-Phosphate (mg/l)	0.67	34.5	0.02	3.5
Total Carbon (TC) mg/l	599.30	1040.0	950.6	NA
Inorg. Carbon (IC) mg/l	238.20	391.8	313.9	NA
TOC = (TC-IC) mg/l	361.10	647.8	636.7	NA
COD (mg/l)	1,411.00	3920.0	1200.0	30
BOD (mg/l)	282.00	784.0	240.0	5
Fe (mg/l)	0.180	0.20	0.26	3.0
Zn (mg/l)	0.330	0.89	1.55	3.0
Cd (mg/l)	0.002	0.11	0.10	0.003
Cr (mg/l)	0.010	0.01	0.10	0.50
Cu (mg/l)	0.010	0.08	0.07	2.0
Ni (mg/l)	0.020	0.05	0.03	0.01
Pb (mg/l)	0.060	0.30	0.06	0.01
Mn (mg/l)	0.010	0.90	1.06	0.40

CONCLUSION

Inga edulis leaf extract contains natural poly-electrolytes that are effective as coagulant and they are very effective for the treatment of petroleum produced water. The degree of reduction effected by *Inga edulis* leaf extract is comparable to the result obtained by Nwaugo *et. al.* 2005. *Inga edulis* leaf extract an inexpensive biocoagulant should be incorporated as a step in the purification of wastewater due to the significant reduction of PAHs and turbidity from produced water. The 1.0g/63µg for 24hr biocoagulant is more effective than 2.5g/63µg for 24hr.

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