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Preliminary investigation on the Extraction of Heavy metals from produced water using *Moringa oleifera* Leaves and Seeds as Adsorbents

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Abstract

The preliminary investigation on the extraction of heavy metals from produced water using M. oleferia leaves and seeds as adsorbents was carried out with a view of sourcing for local or natural absorbents that can be used to treat waste water. The mode of extraction applied was the batch extraction method using dried ground leaves and seeds of the plant that spans through 3, 6 and 9 hours at the end of which the filtrate were analysed for Na, Fe, Zn, Mg, K and Ca using Atomic Absorption Spectrophotometer. The study has shown the effectiveness of the extraction of Na, Fe and Zn by the seeds and leaves of the plant due to the high positive extraction efficiency of these metals. The negative extraction efficiencies of Mg, K and Ca recorded in this study indicates that the leaves and seeds of the plant are not effective in the extraction of these metals. However, there is need to carry out more investigation under controlled laboratory conditions as the plant has potentials in extracting metals.

Keywords: Heavy metals, *M. oleifera*, Hydrocarbons.

Introduction

Man's quest for technological advancement over the years has generated a lot of waste that has greatly affected our natural environment[1,2]. It is one thing to seek for possible means of economic advancement among the committee of nations and another thing to carefully manage the products of such ventures, so as to sustain such developmental bids. Unfortunately in most developing countries including Nigeria, partially or untreated wastes are indiscriminately discharged into the open environment. For instance World Bank reported that about 19,000 tons of hazardous waste is produced annually in Nigeria and the waste comes mainly from steel, metal processing, pharmaceuticals, textiles, tanneries and oil refining industries[1].

Produced water which is one of the major wastes generated in the oil and gas industry is mainly salty water trapped in the reservoir rock or introduced into it and brought up along with oil or gas during production; it can contain very minor amounts of chemicals added down hole during production[3]. These waters exist under high pressures and temperatures, and usually contain contaminants such as hydrocarbons, salts, heavy metals, radionucleotides and ammonia[4]. Laboratory bioassays indicate that both produced waters[5,6] and inland receiving waters[7] cause toxicity in the tests organism *Ceriodaphnia dubia, Fathead minnow*, *Pimephales promelas*, due to major inorganic ions and hydrocarbons. Because of this, they must be treated prior to being discharged overboard in offshore operations or channelled into make shifts borrow pits in the onshore operations. Many chemical constituents found in produced water can either individually or collectively, when present in high concentrations present a threat to aquatic life when they are discharged offshore or to crops when the water is used for irrigation onshore. Produced water can have different potential impacts depending on where it is discharged. For example, discharges to small streams are likely to have a larger environmental impact than discharges made to the open ocean by virtue of the dilution that takes place following discharge.

The principal trace inorganic constituents that are perceived to be of environmental concern are trace metals. Produced water generated from early production has significantly higher trace metal content than that from mature fields. It has also been suggested that corrosion of galvanized equipment could be a source of zinc and lead in some produced waters[4]. Metals exist in lower oxidation states in produced waters that have not been in contact with oxygen, but once such waters are discharged into the environment the metals will oxidize rapidly in the water column. For example, dissolved iron (Fe^{2+}) will undergo rapid oxidation to Fe^{3+} and then form insoluble oxyhydroxides that will precipitate. Many cationic metal species will undergo similar transformations and will co-precipitate either as oxyhydroxides or alternatively as insoluble sulphates (or perhaps sulphides) or carbonates. Hydrogen sulphide present in produced water will oxidize rapidly to elemental sulphur and will precipitate from solution[8].

In managing produced water, the primary alternatives being used today are underground injection, discharge and beneficial reuse, although some other options are used at selected location.

Historically, produced water was managed in ways that were most convenient or least expensive. Several studies on using natural coagulants produced or extracted from microorganisms, animals and plants have been carried out[9, 10]. Among all the plant materials that have been tested over the years, the seeds of *Moringa oleifera* have been shown to be one of the most effective primary coagulant for low cost water purification with potential usage on a large scale in tropical developing countries[11-16].

Recently, there is an increasing trend to evaluate some indigenous cheaper material for wastewater treatment. Since the conventional procedure of wastewater treatment has some disadvantages, such as incomplete metal removal, high cost and high energy requirements, biological materials have been recognized as cheap substitutes for wastewater treatment. Current studies report that *M. oleifera* seeds and pods are effective sorbents for removal of heavy metal and volatile organic compounds in the aqueous system[17,18].

It is based on this background that we set out to examine the use of the seeds and leaves of *M. oleifera* to extract some heavy metals from fresh and stale produced water.

Material and Methods

The fresh seeds and leaves of *M. oleifera* was bought from the Shopping mall at the Rivers State Secretariat complex, Port Harcourt. The samples were washed thoroughly with water and then rinsed with deionised water and oven dried at 105.0^{o}C for 24 hours, before shielding and grinding them in a mortar using pestle. The samples were then sieved in a 1.0mm sieve and was later used for the analysis. The produced water samples used in this study were collected from Nigerian Agip Oil Company limited facility at Ebocha oil centre in Okwuzi in Ogba/Egbema/Ndoni Local government area of Rivers State. Two types of produced waters were collected from the facility. The first one was the fresh produced water which was collected from the outlet of the facility before getting to the make shift borrow pit. Whereas the second one (stale produced water) was collected from the borrow pit.

Three separate 250.0ml beakers were labelled for each set of sample and 2.0g each of the dried powdery leaves where weighed and placed in each beaker; 100.0ml of the fresh produced water were then poured into each set of beakers (nine altogether for a set). The first set was agitated for three hours; the second set was for six hours while the third set was for nine hours using Gollenhamp laboratory shaker. This procedure was followed for the powdery seeds and also for the stale produced water. Note that for each of the produced water type (fresh and stale) there was a set of control wherein the biocoagulant was not added. At the end of each duration the mixture was filtered and the filtrate digested using nitric and hydrochloric acid[19,20]. Aliquot portions of the digests were aspirated into Buck Scientific (205A) Atomic absorption spectrophotometer one at a time. At all stages from sampling to the final determination point, care was taken to avoid contamination of samples and to minimise loss of analyte by adsorption onto the walls of the containers.

All statistical analysis was carried out with the aid of Data Analysis Toolpak in Microsoft office Excell 2003© and SPSS. Differences in the levels of the metals within and between the media were separated by Duncan Multiple Range Test (DMRT) at 95% level of probability[21].

Results and Discussion

The results of the study on the use of *Moringa olefera* leaves and seeds as adsorbents for the extraction of heavy metals from produced water is as presented in figure-1 and 2, while table-1 shows the extraction efficiencies of the metals - Na, K , Ca, Mg, Fe and Zn. From the results the values of Na, Fe and Zn in both untreated produced waters (Fresh and Stale) have higher values than those treated (with both leaves and seeds of the plant) for 3, 6 and 9 hours, whereas the values for K, Mg and Ca are lesser in both untreated produced waters (Fresh and Stale) than the treated ones for the leaves and seeds of *M. olefera.*

Again the extraction efficiencies of the metals as shown in table-1 indicate positive efficiencies for Zn, Fe and Na whereas those of Ma, K and Ca showed negative extraction efficiency. The trend of the extraction efficiency for the metals are Fe>Zn>Na for both seeds and leaves in the treatment of both fresh and produced waters.

From the table-1, Fe and Zn seem to have higher efficiencies in the seeds than in the leaves. This implies that the seeds contain lesser concentration of Fe, Zn and Na while Mg, K and Ca are more in the seeds. This could be the reason why Mg, K and Ca exhibits negative extraction efficiencies, whose trend is Mg>K>Ca. From figures-1 and 2 Mg, K and Ca are more in the leaves than in the seeds of the plant.

Pakade *et al.,* observed higher concentrations of Ca (18500 mg/kg) and Mg (5500 mg/kg) in the leaves of *Moringa oleferea* than selected vegetables (spinach, cabbage, cauliflower, broccoli and peas). Again Ogbe *et al.,* observed the levels of Ca, Mg and K in *Moringa oleifera* leaves harvested from Lafia, Nigeria to be 1.91% ±0.08, 0.38 ±0.01 and 0.97% ±0.01 respectively. While Mutayoba *et al*., reported Ca, Mg and K contents of *M. olefera* to be 2.47%, 1.03% and 1.63% respectively, which are higher than those reported by Ogbe et al., in Ca, Mg and K and Pakade et al., in Ca and Mg in the same plant. These variations may be explained by different climatic conditions, time of the year and different soil types, different growth rate and the stage at maturity prior to harvesting[23].

Table-1
Extraction efficiency of the metals expressed in percentage

Treatments	Na	K	Ca	Mg	Fe	Zn
F PW seeded (3hrs)	13.5	-446.7	4.7	-229.4	100.0	99.5
F PW seeded (6hrs)	18.0	-649.2	-168.5	-146.1	100.0	99.6
F PW seeded (9hrs)	14.9	-422.9	59.5	-154.6	100.0	98.3
F PW leafed (3hrs)	28.3	-844.5	-3011.8	-1458.3	5.9	98.3
F PW leafed (6hrs)	18.7	-217.9	-8321.0	-447.3	28.6	98.4
F PW leafed (9hrs)	12.9	-1007.6	-3328.2	-1576.0	17.7	97.6
S PW seeded (3hrs)	9.2	-1188.7	0.0	-8486.0	100.0	99.8
S PW seeded (6hrs)	8.0	-1212.1	14.7	-6602.0	100.0	100.0
S PW seeded (9hrs)	-41.7	-1162.4	-16.0	-21172.0	54.0	98.7
S PW leafed (3hrs)	5.9	-2192.7	-1488.8	-20676.0	-68.0	98.7
S PW leafed (6hrs)	4.6	-1519.5	-1415.4	-24300.0	100.0	96.4
S PW leafed (9hrs)	-2.0	-1696.1	-1755.6	-50154.0	100.0	97.2

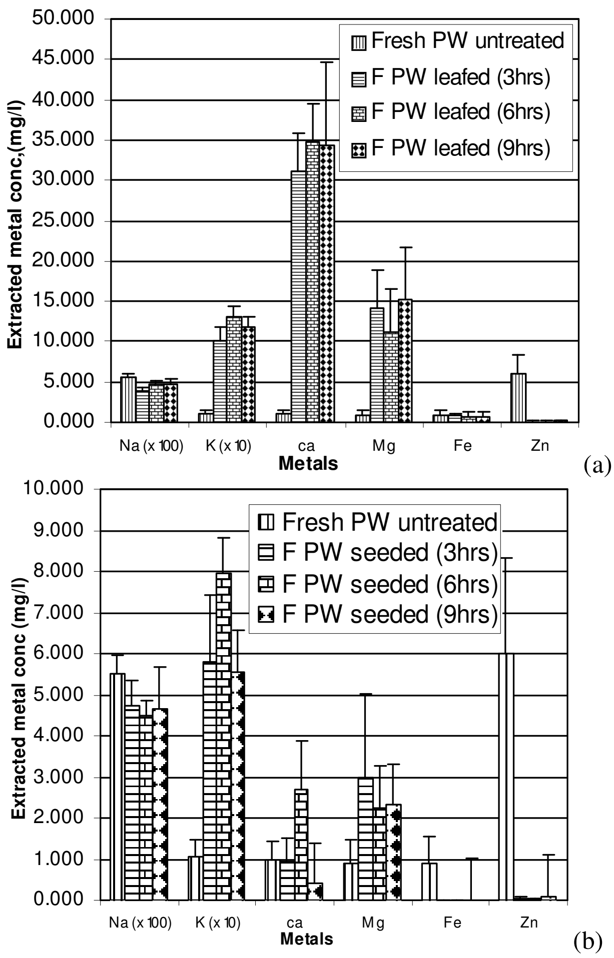

Figure-1
Levels of heavy metals extracted from the treated and untreated fresh produced water using (a) leaves and (b) seeds of *M. oleferia*

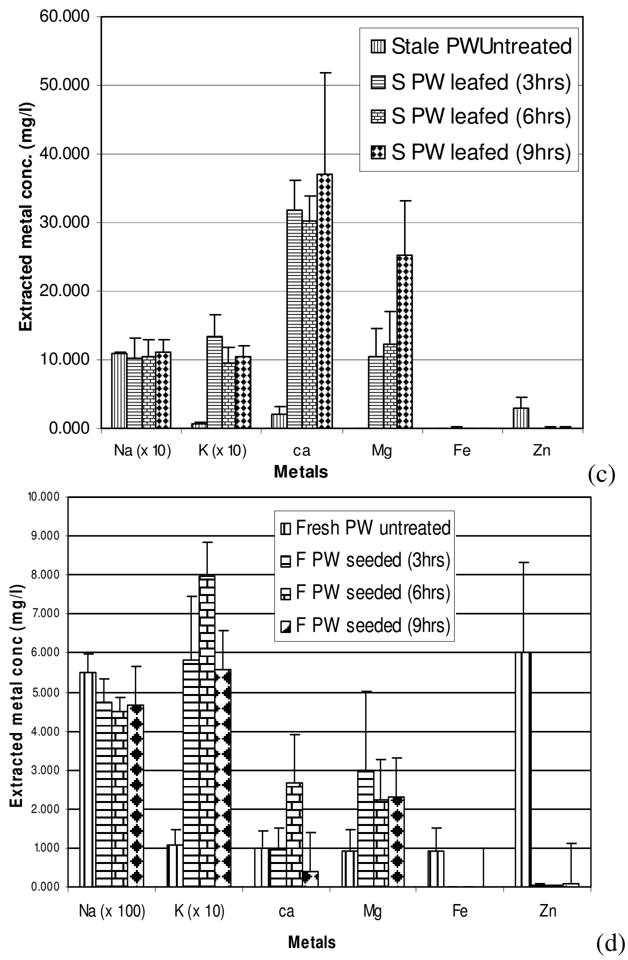

Figure-2
Levels of heavy metals extracted from the treated and untreated stale produced water using (c) leaves and (d) seeds of *M. Oleferia*

However, these high levels of Ca, Mg and K in the leaves of the plant could have lead to the increase of these metals in the treated waste water that lead to negative extraction efficiencies implying that the leaves of the plant and even the seeds cannot be effective in the extraction of these metals based on the method used in this study. For instance K is an important macronutrient and the most abundant cation in higher plants as it is essential for enzyme activation, protein synthesis and photosynthesis, and it mediates osmoregulation during cell expansion, stomatal movements and tropisms. Furthermore, K is necessary for phloem solute transport and for the maintenance of cation:anion balance in the cytosol as well as in the vacuole[23]. The abundance of K in the plant under investigation explains the high levels of this metal in the treated produced waters (Fresh and Stale). Hence, the plant as it was used in this study cannot be used to extract K from the produced water. However to prove these assertions there is need to do more investigations on the use of this plant to extract these metals under controlled laboratory conditions. This finding corroborates the assertions in some literatures for instance the 'Tree for life Organisation' that "ounce-for-once, moringa leaves contain more calcium than milk, more iron than spinach and more potassium than bananas", and that the protein quality of moringa leaves rivals that of milk and eggs. However in a related study Jahn *et al*.,[25] in their studies has asserted that *M. oleferia* seeds can be an alternative for water treatment, especially in developing countries to reduce costs and expand water supplies in rural areas, although no large scale exploitation has yet been performed.

Ogbe *et al.,*[23] reported the levels of Na, Fe and Zn in the leaves of *Moringa oleifera* to be 192.95 ± 4.48, 107.48 ±8.81 and 60.06 ± 0.30ppm respectively. While Mutayoba *et al.,* reported the levels of Fe and Zn in the same plant but from a different location to be 318.81ppm and 21.70 ppm respectively. The levels of these metals Na, Fe and Zn are lower than those of Ca, Mg and K in the leaves of the plant. This could be one of the reasons why their extraction efficiency is far higher than those of Ca, Mg and K both in the leaves and seeds of the plant. Several researchers have reported that the aqueous seed extract has been traditionally used to purify water in Africa and in South Asian countries, as a natural coagulant since it has high levels of active cationic proteins with molecular mass between 6 and 16kDa and highly alkaline isoelectric points[14,25,26,27] with a coagulation efficiency similar to that of alumen in samples with high turbidimetry[25].

Conclusion

The study on the preliminary investigation on the extraction of heavy metals from produced water using *M. oleferia* leaves and seeds as adsorbents has shown the effectiveness of the extraction of Na, Fe and Zn by the seeds and leaves of the plant due to the high extraction efficiency of these metals. The negative extraction efficiencies of Mg, K and Ca recorded in this study indicates that the leaves and seeds of the plant are not effective in the extraction of these metals. However, there is need to carry out more investigation under controlled laboratory conditions as the plant has potentials in extracting metals.

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