American Journal of Engineering Research (AJER)
e-ISSN: 2320-0847 p-ISSN : 2320-0936
Volume-10, Issue-9, pp: 01-07
www.ajer.org
Research Paper Open Access

Reducing the Impact of Toxicity of Refinery Effluent Using Seed Extract and Micro Porous Carbon from Seed husks of Moringa Oleifera

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ABSTRACT
Contamination of the environment with industrial chemicals and/or effluent has become a major problem. In this study, the toxicity of a refinery effluent was tested by exposing a commonly occurring invertebrate, Chironomus sp. (early larva stage) using the 96-h static bioassay to establish the LC_{50} value. Seed extract from a widely distributed tropical plant, Moringa oleifera was used to treat the effluent employing a modified laboratory jar test procedure. Hardness and alkalinity were reduced to between
19 and 30% with reduction found to be dose-dependent. Adsorption isotherms were established and were found to approximate the Langmiur type ($IQ = 1Q_o X l/Q°C$). Char from M. oleifera seedhusks was also used to test the sorption of toxicants. A single toxicant from the effluent phenol, was used for sorption studies using pseudo-equilibrium batch contact experiments. Sorption was found to obey a Freund lich type adsorption isotherm (of the form q =KC). Retesting the toxicity of the effluent by re-introducing a different set of the test organism after treatment yielded no significant mortality. Moringa oleifera seed extract, char and possibly activated carbon from seed husks hold a promise to further reduction of the toxicity of refinery effluent

KEYWORDS: effluent ,toxicity, adsorption, moringa oleifera, suspended solids, hardness, mortality, extract , phenol and concentration

Date of Submission: 21-08-2021 Date of acceptance: 05-09-2021

Notations

$LC_{50} =$ median lethal concentration responsible for 50% population kill
$S \log_{10}LC_{50}$ = standard error of LC_{50}
a = slope of the log-dose probit response line
p = number of concentration levels or treatments.
M =number of shironomus in each treatment
w = the average weight of the observation
$Q_s =$ratio of hardness adsorbed to the dosage of M oleifera seed extract
$Q^{O} = -$ adsorption kapasity of M. oleifera and for carbonized husks k be taken as Langmuir monolayer coverage constant
b — Langmuir adsorption coefficient (a constant related to energy of the adsorption).
k_e or k = residual solution phase onentration amount of phenol adsorbed per unit weight.
K = freundlish constant (mol g^{-1}).

n = freundlish constant(relates to the enthalpy of adsorption whih actually describes the intensity of the reaction).

I. INTRODUCTION

Oil has established itself as the major source of revenue for Nigeria since 1970 and there has since been a steady growth in the petrochemical industry of the nation. It is therefore no secret that environmental impacts associated with oil operations have also increased. Several toxic components of oil were identified by Cote (1996) who also identified the following toxicants from petroleum refinery effluent, oil and grease, cyanide, sulphides, compounds of nitrogen, ammonia, heavy metals like Cu, Cr, Fe, Cd, Mo, Pb, Ni, Se, Va and Zn and high amounts of suspended solids. Oladimeji and Onwumere (1986) analyzing several batches of effluent collected over a period of eight months from NNPC Kaduna Refinery confirmed the presence of the above components. Charlesba (1998) working on the toxicity of Port Harcourt Refinery effluent also identified most of theabove components as being present in the treated effluent.

Refinery products and processes constitute a very important source of oil in the Nigerian aquatic ecosystem, most especially due to the fact that some of the refineries are located near the coastal areas and discharge their effluent directly into coastal waters. Those that are located in the hinterland such as that of Kaduna discharge into freshwater ecosystems. Based on the fact that most of these components are toxic, they therefore affect valuable resources (Sprague, et. al; 1978, Onwumere, 1986 Oladimeji 1987, Omorigie, et. al; 1995, Charlesba, 1998).

Oladimeji and Onwumere (1986) compared the composition of refinery effluent, from NNPC Kaduna and concluded (based on the level of major toxicants remaining in the treated effluent) that the standard of treatment compared well with what obtains in developed nations. However, studies (Oladimeji, 1985 Onwmere, 1986 Omorigie, et. al ; 1995 and Charlesba, 1998 Charlesba, et. al; 1998) have shown that the effluent still remains toxic both to invertebrates and vertebrates Knowing the LC_{50}, (the median lethal concentration that kills50% of test organism) is not an acceptable goal to control toxicity in a receivmg ecosystem (Welch, 1992). Reducing the toxicity to a level that will allow complete survival of all the life stages of the animal's life history, referred to as 'safe concentration' is preferred.

Legislation protecting the environment are becoming more and more stringent and are expected to become even tighter as more people in developing countries become environmentally conscious. If we are to satisfy the laws protecting the environment and at the same time not compromise the much desired sustainable development, then local and effective technoologies peculiar to our problems beevolved. Moringa oleifera (family Moringaseae) is a tree species endemic to the whole tropical belt and abundantly found in the Northern part of the Country. Apart from its use for a variety of purposes (leaves as food, roots for medicine), seed extract is used as a natural coagulant (McConnachie, 1993, Pollard, et al; 1995), softening of hard water (Muyibi and Evison, 1995) and has been found to be non-toxic and biodegradable (Ndabigengsere, 1995). Generally, activated carbon can be produced from any carbon-based material.

However, commercial activated carbons are expensive and their use justified only in the recovery of a valuable material or product. There is therefore the need to produce cheap carbon that could be effective in the treatment of water, waste water and trade effluents.

II. MATERIAL AND METHODS

***Chironomus Sp*.**

The Chironomus sp. were collected fromsome selected local government in the Niger Delta, in open aquaria tanks (50cm x 50cm) and brought to the Hydrobiology Laboratory of the Department of biological Sciences, Niger Delta University, Ammasomma, Yenegoa, Bayelsa State. The animals were maintained in the Laboratory for a period of two weeks at 25 +- 2°C and under natural photoperiod.

Refinery effluent

Effluent were collected from the out-fall point of The treatment plant in thoroughly washed 20L capacity plastic cans in the early hours of the morning (between 6am and 11 am). At collection site, hardness (mg/l of $CaCo_3$), alkalinity (mg/l $CaCo_3$), pH, dissolved oxygen, and temperature were determined following the methods of APHA (1985). Phenol content was however later determined in the Laboratory (APHA, 1985) at the Department of Biological Sciences, Niger Delta University.

Acute Toxicity Test

The interstar stage of Chironomus sp. were exposed to acute concentration of refinery effluent for 96 hours in static bioassay experiment. Effluent concentrations of 20, 40, 50, 60, 80 and 100% v/v were made using dechlorinated Ammasomma Community Water. A control experiment was set up with only the dechlorinated water. Each concentration was replicated. Ten individuals each were randomly distributed to each test tank and concentration in each test tank renewed after 48 hours. Observation for mortality was done at 15, 30 minutes and at 1, 2, 4, 6, 12 and 24 hours after which observations were only done twice daily till termination of the experiment (at 96-hours). An organism was considered dead when all forms of movement seised and the organism was either laying still on the bottom or coiled up and a gentle prodding elicited no response. Dead individuals were removed from the media and death recorded. The probit method was used to establish the 96-h LC_{50} value and 95% confidence limit (Finney, 1964 Dick and Dixon, 1985)

Seed extract

Dry M. oleifera seeds (from Pods dried on the plant) were obtained from the Botanical garden of the Biological Sciences Department, Niger Delta University, and the active ingredient extracted based on the method of Muyibi and Evison (1995). Seed husks were manually removed and seed ground to powder with a Glen Creston blender. 2g of the powder was then dissolved in 200m1 distilled water and mixed using a mixer for 30 seconds. The suspension made was filtered with a muslin cloth and the filtrate made up to 500m1 with distilled water. The resultant solution gave approximately 4000mg1^{-1} of stock solution.

Preparation of Carbon from Seed husks

Pollard, et al; (1995) studied the thermal properties of M. oleifera seed husks and based on his findings, a temperature of 450°C and dwell time of 10 min. was used for the carbonization of the husks. Successive charges, 5g each of finely divided seed husks were put in a Cabolite furnase, in combustion boats. After 10 minutes, the char was removed, desiccated (by putting in a desicator) and gasified with steam at delivery rate of 5cm^3 min $^{-1}$ for 30 minutes. The gasified char was cooled in a desiccator, homogenized by slight pounding and sieved with a sieve of<250 pore size. The char was then washed with 80cm^3 of 2M HCL (Pollard, et.al ; 1995) and rinsed twice with 80cm^3 of deionized water using vacuum filtration. Oven drying of the remaining char was done at 60^{o}C for 24 hours.

Seed extract experiment

500ml of the treated refinery effluent was put in a 1 litre capacity beaker and mixed using the paddle of a jar apparatus at a mixing speed of 115 rpm. The required amount of M oleifera seed extract (50ml,100 ml, 150m1 and 200m1) was added to the beaker and mixed for 2 minutes. A setting time of lhr was allowed after which the flocks were filtered and residual alkalinity measured according to APHA (1985).

Phenol adsorption Text Using Char

Pollard, et. al; (1995) established that for a steady state adsorption to be attained, a contact time of 24hr is required. Also, measurement of effluent pH was found to range between 5.6 and 7.4 and this range assured the predominance of undessociated form of phenol (Ward and Getzen, 1990). 0.5g of carbon was put in II effluent containing 1.07 m mol 1^{-1} and agitated at 450 rpm in a thermoslated bath at 25 ± 2°C. 500ml of the effluent were withdrawn at specific intervals (hours) and filtered using Whatman filter paper and phenol concentration analysed using methods given in APHA(1985).

Calculations

The 95% contidence limit, CL, of 96-h LC_{50} of Chironomus sp. exposed to treated refinery effluent is given by the standard error equation:

$S \log_{10} LC_{50} = 1/a$ square root(pmw)…………………..(1)

This is then substituted Into:

Log_{10} (95% C.L) = $Log_{10} LC_{50}$ +- 1.96 ($S \log_{10} LC_{50}$) .... (2)

The adsorption behaviour of seed extract is given by the Langmuir adsorption isotherm described by equation 3.

$I/Q_e = I/Q^o + I/bQ^o S_e$……………………………………(3)

while equation 4 is a simplified Freundlich expression that describes the data fit for the pseudo-equilibrium seed husks.

q= KC………………………………………………………. (4)

III. RESULTS AND DISCUSSION

Mortality indices of Chironomus sp. exposed to treated refmeiy effluent of 96-h LC50 value are presented Table 1. Percentage mortality when transformed into probits and plotted against the log-dose of the effluent gave a linear relationship as shown in figure 1. From figure 1, the 96-h LC_{50} determined is 46% v/v with a 95% confidence limit
range of 45.9157 - 46.08424 (using equation 1 and 2). The slope function is 3.11.

Table 1. 96-h mortality indices for Chironomus sp. Exposed to treated refmery effluent.

Effluent conc. %	Mortality v/v ratio	% Mortality mortality	Probits of observed	Expected probits	Weights (w)
20	8/20	40	4.7467	4.20	0.503
40	9/20	45	4.8743	4.80	0.627
50	11/20	55	5.1257	5.10	0.634
60	14/20	70	5.5244	5.40	0.601
80	16/20	80	5.8416	6.20	0.370

100	20/20	100	-	6.80	o.180 Ew =2.915 W = 0.4858

According to Lloyd (1991) mortality of organisms exposed to crude oil is as a result of the crude acting as a barrier to oxygen uptake. This eventually lead to increase in ventilation rate subquently increasing the amount of toxicants taken in. Refinery effluent contain oil and grease (Onwumere, 1986). Death of the test organism could have been as a result of ventilation impairment by oil and grease blocking the ventilation surfaces or could equally have been a more direct effect of one, a few or several of the toxicants on body physiology. Results of hardness removal by seed extract (suspension) from M. oleifera are shown in Figure 2

Hardness was found to have been removed to between 19 and 30%. Removal of hardness was observed to be dose - dependent. A maximum dose of 200mg l^{-1} was administered and though no total hardness removal was recorded it may be possible that higher doses could have led to zero value of hardness. Rate of hardness removal was found to be higher at lower doses than at higher doses. In this study no magnesium hardness was measured, but Muyibi and Evison (1995) softening hardwater with extracts from M. oleifera seeds observed that Ca hardness was removed at a faster rate

than hardness due to Mg ions. Weber (1972) had earlier observed that Ca is selectively adsorbed in preference to Mg ions due to smaller hydrated radius. It is therefore possible that higher doses could have led to Mg ions removal as well. M. oleifera has been shown to be a natural cationic polyelectrolyte and flocculent and contains up to six amino acids (Jahn, 1986). These amino acids are mainly glutamic, methionine and arginine. As a polyelectrolyte, it Is entirely possible that the mechanism of hardness removal by M. oleifera from the effluent could b by adsorption and interpartikle bridging as was postulated by LaMer and Healy (1999).

Adsorption isotherm developed for hardness removal is illustrated in Figure 3 and was found to approximate the langmuir type. phenol sorption experiment with carbonised seedhusks show adsorption isotherm illustrated in figure 4 and represent a characteristic monolayer absorption. Under the concentration range that was investigated (<1.3 mol$^{\cdot -1}$), a simplified Freundlich expression, q= KC_ fitted the data adequately.

Streat et.al; (1995) investigated the sorption of phenol and P- chlorophenol from water using conventional and novel activated carbons and found a similar expression that describes the sorption behavior. Goto, et. al; (1986) had earlier investigated the sorption of phenols from water and found a similar form of sorption isotherm.

Several mechanisms of phenol adsorption on carbon have been suggested. Coughlin, et. al; (1998) suggested that the sorption involves dispersive forces between the electrons in the phenol and those in the carbon and that phenol adsorption decreases with increasing oxygen loading to carbon due to complex formation Mattson et. al; (1999) suggested a donor - acceptor mechanism in which the carbonyl oxygen group on the carbon act as electron donor where as the aromatic phenol ring act as the acceptor.

A fresh set of the test organism were exposed to the effluent treated with the seed suspension and carbonized char and no significant mortality - with only one death out of the several organisms introduced recorded and this was in the 100% effluent concentration. Though only hardness and phenols were measured and the results showed their reduction, it is Suspected that other toxicants contained in the effluent such as oil and grease, metals among others might have been reduced and/or removed from the effluent. Toxicity of pollutants is affected by several factors prominent among them is hardness (Ca + Mg), which for instance in fish, inhibits competitively toxic metals at gill sites. Pagenkopf (1983) was of the view that competition is more effective if hardness is >1mM (100 mg l^{-1} $CaCo_3$). The hardness considered here is >1mM (actually 110mgl $^{-1}$). Removal of these metal (Ca^{2+} and $Mg^{2+)}$ species by the seed suspension would invariably involve the removal of other toxic species.

Industrial effluents are highly complex. Mixtures of toxicants can display either additive, antagonistic or synergistic toxic effects. The synergistic effects of heavy metals in refinery effluent on living organisms, that is zinc in combination with copper and lead, copper and phenols in combination with low oxygen have been reported (Lloyd, 1991). Reduction in the concentration of phenols by Char from M. oleifera seed husks would have led to the reduction of the synergistic effect and hence reduction in toxicity.

IV. CONCLUSION

Results show that the toxicity of refinery effluent can be reduced using seed extracts and char from seed husks of Moringa oleifera. Further research is however
rekommended in the study of the mechanisms involved in the toxicity reduction processes.

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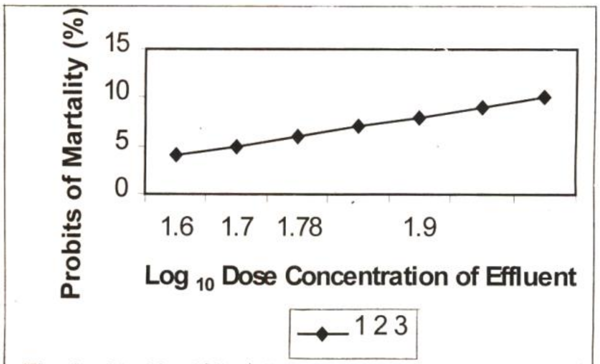

Fig: 1. Probit of Mortality versus log-dose of effluent

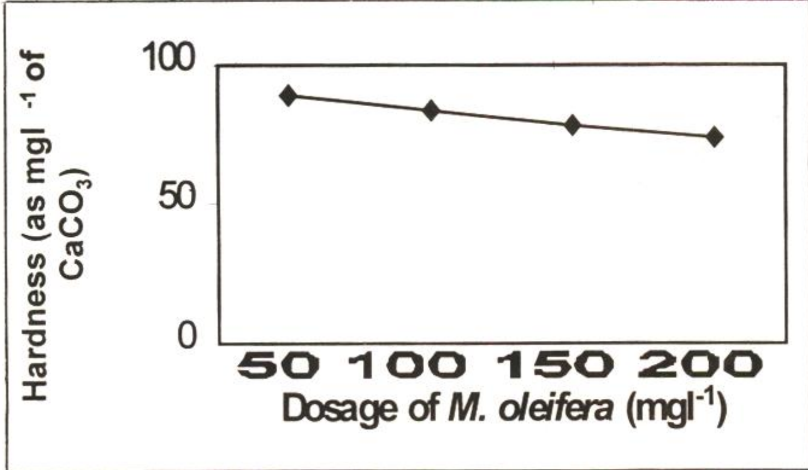

Fig:2 Showing Hardness (as mgl^{-1} $CaCO_3$) removal by *M. oleifera* seed suspension.

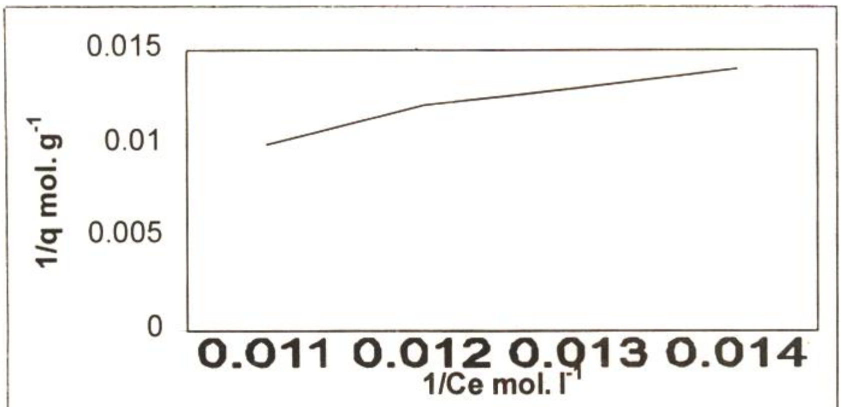

Fig:3 Showing the Langmuir adsorption isotherm fit for *M. oleifera* seed suspension.

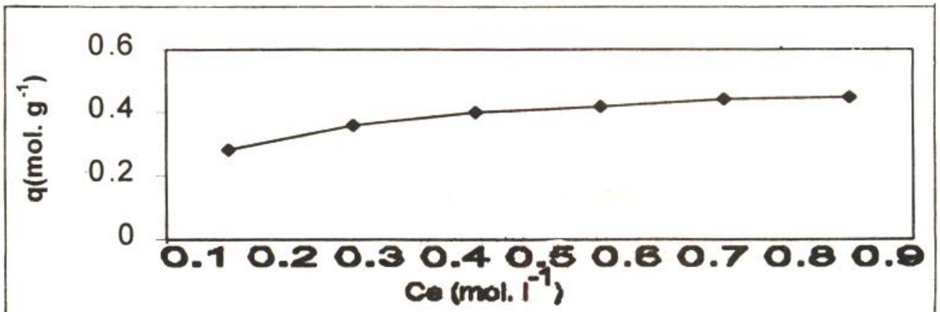

Fig:4 Pseudo - equilibrium isotherm of phenols at 25 + 2°C on Carbonised seed husks (char) from *M. oleifera*. Note: Curve represent the $q = KC^n$ Freundlich fit.

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Akpoturi Peters. "Reducing the Impact of Toxicity of Refinery Effluent Using Seed Extract and Micro Porous Carbon from Seed husks of Moringa Oleifera."*American Journal of Engineering Research (AJER)*, vol. 10(9), 2021, pp. 01-07.