Available online at www.scholarsresearchlibrary.com

Scholars Research Library

European Journal of Applied Engineering and Scientific Research, 2012, 1 (4):190-195
(http://scholarsresearchlibrary.com/archive.html)

ISSN: 2278 – 0041

Removal of Heavy metals from Produced Water Using of Biosorption techniques

Aka Chidike Kanu†, Akuma Oji §

†Sunlink Petroleum Limited, 7a Taslim Elias Close, P.O. Box 72049, Victoria Island, Lagos, Nigeria,
§Department of Chemical Engineering, University of Port Harcourt, Rivers, Nigeria

---

ABSTRACT

Oil and grease, temperature, pH, and heavy metal concentrations are some of the main quality parameters used in the regulation of the discharge of oil and gas field produced water to the environment. The use of cheap biological plant materials to selectively remove heavy metals from aqueous solutions is considered a potentially viable alternative to expensive ion-exchange resins and semi-permeable membranes. However, a key requirement for the efficient and cost-effective application of biosorption systems to industrial-scale wastewater treatment is the ability to regenerate and reuse biological sorbents used for the ion uptake. This paper presents a case study of the application of biosorption to sample produced water from an oil field in the Niger Delta. The produced water was characterised for both heavy metal concentration and other quality indices. Using batch adsorption system, with raw and pre-treated sawdust as adsorbent, uptake of heavy metal ions was investigated. The analyses indicated that the sorbent samples have significant sorption capacity for heavy metal ions. Applying classical equilibrium sorption model and theory, it was observed that metal ion affinity as a function of reversibility of adsorption, was very sensitive to biosorbent pre-treatment used. Based on this case study, a cheap and simple process for the tertiary treatment of produced water is proposed. Further investigation is envisaged in the area of continuous-flow system modelling and optimisation.

Keywords Produce formation water • Effluent • Biosorption • Saw dust

---

INTRODUCTION

Environmental Impact of industrial activities and reprisal activities of stakeholders and public institutions has giving raise to a state of crises or near crisis in several regions where projections are not made to monitor, prevent or reduce effect of industrial effluents on the host environment and communities. Environmental Impact assessment and Sustainable development are now keywords in all industrial project aim at creating a balance between risks, socio-economic and environmental considerations in the design, construction, Installation and operation of technological facilities.

The Niger delta region of Nigeria is a region of high Petroleum production activity. The region is currently laden with incessant interference on economic activity due to issues of sustainable development with stakeholders. One of the visible impacts pointed at is the effect of the effluent discharge from Oil Production platforms into rivers and estuaries (Gberesu, 1989). These affect host communities of these production activities when eat fish from the rivers or drink contaminated water. International Occupational Safety and Health Information Centre in her journal (1999) stated that Heavy metal toxicity can result in damaged or reduced mental and central nervous function, lower energy levels, and damage to blood composition, lungs, kidneys, liver, and other vital organs. Formation water is natural occurring water which in some cases and found in association with oil and gas bearing rocks in oil formations or reservoir (Kobranova 1989).

Natural Gas and Formation water are the major byproducts of the Crude Oil Production Industry. Crude Oil, a mixture of Oil, gas and water flows from the reservoir through pipelines to the platform where the mixture is separated. The Natural gas is flared until the resent Government program to stop flaring. The water from the separation process which is known as process water is usually discharge after biological treatment in an oxidation pond.

The Federal Ministry of Environment, Nigeria Conservation Foundation noted that The damage from oil and gas operations is chronic and cumulative, and has acted synergistically with other sources of environmental stress to result in a severely impaired coastal ecosystem and compromised livelihoods and health of the regions impoverished residents. The 70,000 square kilometers Niger Delta contains 7,400 of West Africa's 20,000 square kilometers of mangroves, and is considered one of the 10 most important wetlands and marine ecosystems in the world. Millions of people depend upon the delta's natural resources for survival, including the poor in many other West African countries who rely on the migratory fish from the Delta. The region contains many threatened species found nowhere else in the world, including several primates, ungulates and birds.

Information on the volume and characteristics of the effluent discharge is difficult to asses due to the non-transparent nature of the Multi nationals working in the Oil Industries.

Several studies including that by Muhammad et tal, (2005) and Lenntech (2006) revealed that drive for proactive attention on effective treatment of waste before discharge from petroleum has been on the increase to encourage the reduction of its impact on the economy of such operation and on the environment.

The use of activated carbons have been determined to be the best available adsorbent due to its low cost, application technology and ability to purify polluted waste streams and removal of many contaminants. (Mangun et al, 1999). Wood with a chemical component of 40~50% Cellulose, 20~30% lignin, 20~25% hemicelllose and 5~10% extraneous material is one of the adsorbent sources classified as biosorbents having adsorbent capacity for metals in solution (Mark et al 1998 and Bain 1993).

The most important parameter for determining the efficiency and cost of adsorbents is the adsorption capacity. Adsorption isotherm is a graphical; representation of the relationship between the amounts of adsorbate adsorb per unit mass of adsorbent and the equilibrium concentration of the solution at constant temperature (Kenedy et al, 1993).

The goal of this study to asses the physioco-Chemical properties of absorbent of biological cellulosic origin, its adsorptive capacity for treatment of formation water and its preference to the untreated material and a universal activated carbon. The parameter of the effluent water under study are the Zinc ion, Chloride ion, Sulphate ion, Sodium, Potassium and the total dissolved solid.

MATERIALS AND METHODS

Sawdust collection and Treatment

The sawdust as the raw material for the production of the modified sawdust was collected for a Jimeta Timber Market, Yola, Northern Nigeria.

Raw Sawdust

The raw material was washed several times using tap water and finally with distilled water, dried and stored at room temperature for further use.

Hydrolyzes Sawdust

The sawdust was soak completely in water and heated between 90~110^{o}C for 30mins. The hydrolyzed wood was thoroughly washed and dried and stored at room for further use.
The two sawdust adsorbents were screened to obtain a uniform particle size (mesh size 0.2 ~ 0.8mm).

Powered Activated Carbon
The Powered Activated Carbon manufactured by Vickers Laboratory Ltd, UK with particle sizes corresponding to an 80-mesh sieve (0.2 mm)

Produce formation water Sample
The Produce formation water effluent sample was collected from Brass Oil terminal of an Oil and Gas processing facility operated by a multination oil and gas production firm Nigeria Agip Oil Company (NAOC) in Brass, Niger Delta, Nigeria.

Biosorption study
The study was carried out in a batch mode. The experiments were carried in batch mode using the different adsorbent (Activated carbon, Sawdust and modified sawdust) under the same temperature condition (room temperature) and constant volume with designated weight.

The adsorption capacity of Heavy metal (zinc) by activated carbon, Sawdust and modified sawdust were measured under the effect of contact time and adsorbent at room temperature (26±2□C) and pH of (9.0±3□C). The residual concentrations were measured using Pye-Unicam SP9 Atomic Absorption spectrophotometer and $AgNO_3$ titration.
The adsorption capacity, were calculated from the difference between the initial concentration and equilibrium concentration.

RESULTS AND DISCUSSION

The Total dissolved Solid concentration of the Produce water analyzed to be 17200mg/l, Zinc concentration of 3.6mg/l, chloride 2.0, Sulphate 12.5mg/l, Sodium 323 mg/l and Potassium concentration of 11mg/l.

Total dissolved Solid (TDS)
Result show that the Total dissolved solid reduced with increasing dosage as reported in Table 1

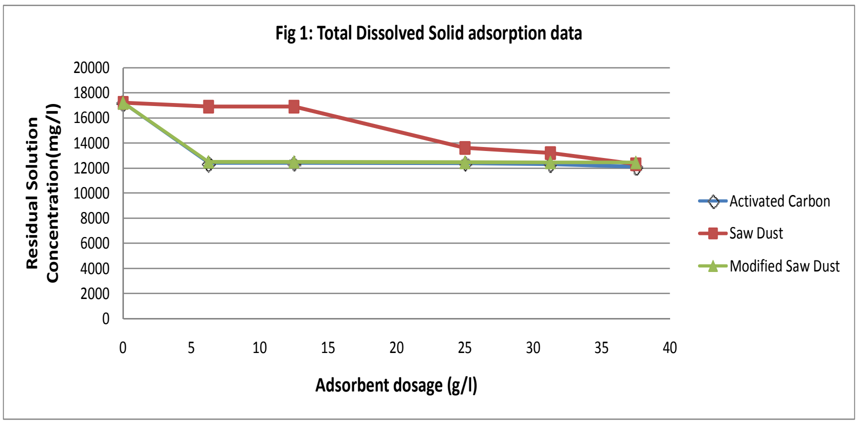
Table 1: Treated Sample Total dissolved Solid adsorption Data

	TDS (mg/l)		
Adsorbent Dosage (g/l)	Activated Carbon	Saw Dust	Modified Saw Dust
0	17200	17200	17200
6.25	12400	16900	12500
12.50	12400	16900	12500
25.00	12380	13600	12470
31.25	12300	13200	12450
37.50	12100	12300	12450

The high value of TDS is an indication salinity of Produce water. There is reduction in the TDS by the adsorbents. The result produced from the use modified sawdust is pronounced due to increased specific volume of the material by hydrolysis of the hemicellulose component of the wood as well as the extraction of the hydrolysate and extraneous materials by the modification process.

The TDS data could not fit into the Freundlich isotherm because of the complex nature of such waste water (Brenner et al, 1993).

A plot of the adsorbent loading against residual solution concentration shows different adsorption characteristics of the adsorbents. Activated carbon should high adsorption capacity for TDS followed closely by the modified sawdust. Sawdust exhibited total solute affinity and least capacity. That depicts that the sawdust will require higher temperature for regeneration and the attendant process application and cost of such regeneration. The adsorption capacities are as a result of larger intricate net work of micro-pores consequent on thermo-chemical treatment. The low affinity of Activated carbon is indicative of predominant polar nature dissolved solids on adsorbents (Kremmer, 1988)



Sodium and Potassium

Potassium ions were adsorbed appreciably by modified Sawdust than activated carbon and sawdust. Adsorption by sawdust was very low. The reason for this in not too clear but my not be unconnected to the low solution concentration.

Table 2: Treated Sample Sodium Analysis and Adsorption Data

Adsorbent Dosage	Activated Carbon		Sawdust		Modified Sawdust	
(g/l)	Absorbance	Conc.(mg/l)	Absorbance	Conc.(mg/l)	Absorbance	Conc.(mg/l)
6.25	320	320	299	300	314	315
12.50	320	320	294	295	310	310
25.00	310	310	310	310	290	290
31.25	320	320	297	297	291	291
37.50	316	316	300	300	280	280

Potassium was adsorbed by the three adsorbents is as shown in table 3. The Result show adsorption of Sodium by modified Saw dust whereas Activated carbon and Saw dust show little or no adsorption. Modified sawdust adsorbed sodium in a relatively highest appreciable amount. This improved performance may be related to the metal ion affinity of lignin and the cellulose micelles incident on hemicellulose hydrolysis and extraction present in biological adsorbents like wood.

Table 3: Treated Sample Potassium Analysis and adsorption data

Adsorbent Dosage	Activated Carbon		Sawdust		Modified Sawdust	
(g/l)	Absorbance	Conc.(mg/l)	Absorbance	Conc.(mg/l)	Absorbance	Conc.(mg/l)
6.25	16.3	8.0	24.0	11.0	16.0	7.5
12.50	16.0	7.5	24.0	11.0	15.0	7.0
25.00	16.0	7.5	23.0	11.0	15.2	7.0
31.25	15.8	7.3	20.0	9.5	12.9	6.0
37.50	15.5	7.0	19.0	9.0	12.0	5.5

Heavy Metal (Pd, Fe, Cu, Cr)

The atomic adsorption spectrometric test indicated the presence of Zinc ion only on the produce water sample.
All the adsorbents adsorbed zinc ions from solution in various degrees. Residual treatment sample concentrations reduced with increasing dosage. See table 4.

The adsorption of zinc from the solution and the equilibrium data fitted into Freundlich isotherm (Figure 3). The adsorption characteristics of the material showed Activated carbon having the higher adsorption capacity at low concentration, less than 1.7 mg/l. how every at concentrations higher than this the adsorption capacity of sawdust has greater affinity, thus for higher concentration the cellulose adsorbents would be more suitable.

Table 4: Treated Sample Zinc sample analysis and adsorption data

Adsorbent Dosage	Activated Carbon		Sawdust		Modified Sawdust	
(g/l)	Absorbance	Conc.(mg/l)	Absorbance	Conc.(mg/l)	Absorbance	Conc.(mg/l)
6.25	0.105	3.20	0.094	2.80	0.085	2.60
12.50	0.095	2.90	0.082	2.40	0.080	2.40
25.00	0.089	2.70	0.080	2.40	0.068	2.00
31.25	0.080	2.40	0.079	2.38	0.065	1.90
37.50	0.076	2.20	0.066	2.00	0.063	1.80

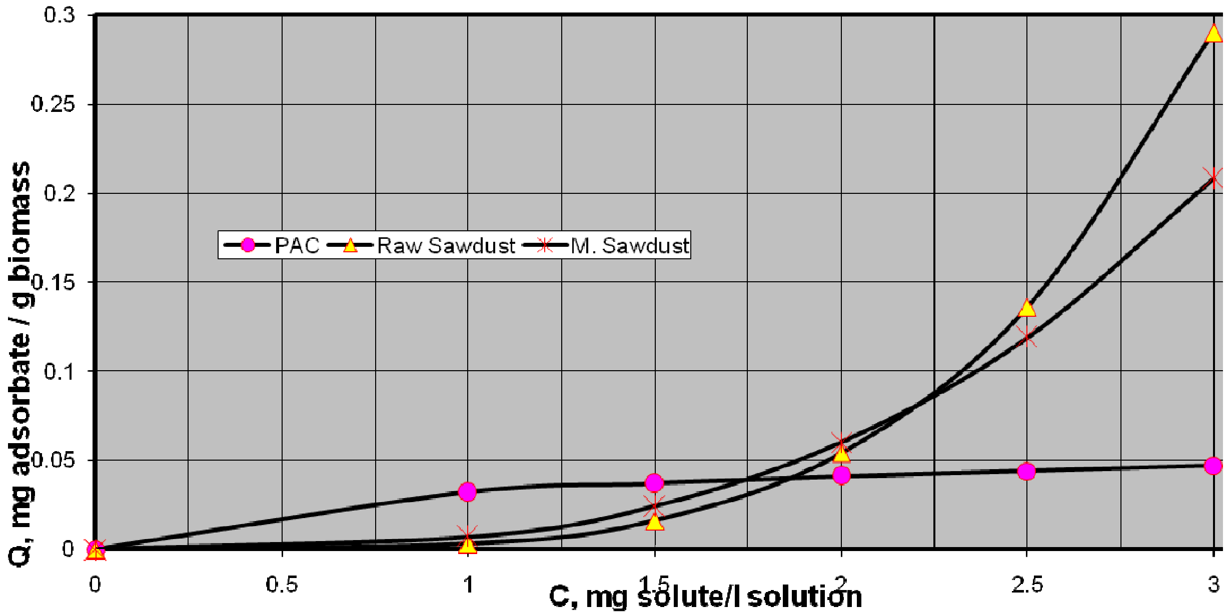


Fig 2: Adsoption (langmuir) isotherm

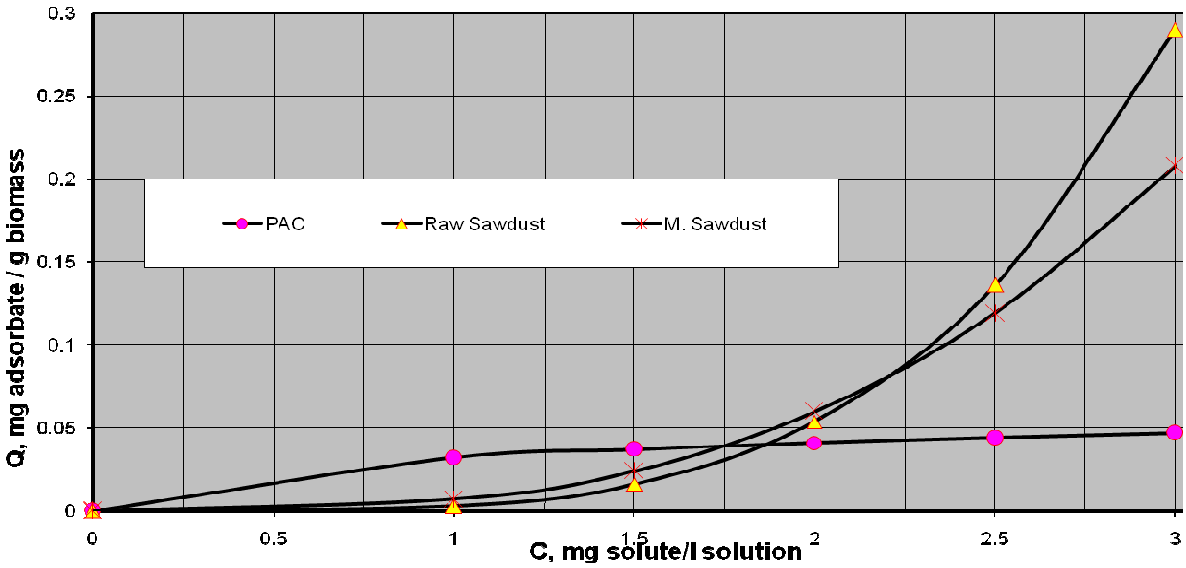


Fig 3: Freundlich Isothgerm

Chloride and Sulphate

Analysis indicated that chloride ions were not removed by any of the adsorptive systems.
All the adsorbents showed various level of sulphate ion absorbance.
Due to the high electronegative of the chloride ion, it is not adsorbed to the adsorbents.

CONCLUSION

The parameters of Produced water from an oil field in the Niger delta, including total dissolved solid, heavy metal (Zinc) and Soduim and Potassium ion concentration in Produce water which are the main quality parameters used in the regulation of the discharge of oil and gas field produced water to the environment has been analyzed and the sample treated with Activated carbon, sawdust and modified sawdust. Result of the analysis has shown that the capacity of this cheap biological plant material to selectively remove heavy metals from aqueous is considered a potentially viable alternative to expensive ion-exchange resins and semi-permeable membranes. However, a key requirement for the efficient and cost-effective application of biosorption systems to industrial-scale wastewater treatment is the ability to regenerate and reuse biological sorbents used for the ion uptake. The thermo-chemical treatment given to the sawdust justified is advantage to raw sawdust in the area of regeneration. The batch adsorption system, with raw and pre-treated sawdust as adsorbent, uptake of heavy metal ions was investigated leaves no doubt to appreciable amount of reduction of pollutant concentration of Soduim and potassium ions. Applying classical equilibrium sorption model and theory, it was observed that metal ion affinity as a function of reversibility of adsorption, was very sensitive to biosorbent pre-treatment used. Based on this case study, a cheap and simple process for the tertiary treatment of produced water is proposed. Further investigation is envisaged in the area of continuous-flow system modelling and optimisation.

REFERENCES

[1] Alam M. Z. , Muyibi S. A and Kamaldin N. Production Of Activated Carbon From Oil Palm Empty Fruit Bunches For Removal Of Zinc \
Retrieved from: http://www.iwtc.info/2008_pdf /5-3.PDF

[2] Bains W., Biotechnology From A-Z, Oxford University Press, Oxford, **1993**.

[3] Brenner A, Belkin S., Utizur S. and Abeliovich A., *Water Science and Technology*, Vol. 27, pp 113-120, **1993**.

[4] Federal Ministry of Environment, Nigeria Conservation Foundation Lagos, Niger Delta *Natural Resource Damage Assessment and Restoration* Project - Phase 1 – Scoping Report (**2006**)

[5] Gberesu D. A. Finding Profits in Oil Well Wastewaters, Chemical Engineering, Vol. 77, pp 165-168, **1989**

[6] International Occupational Safety and Health Information Centre (**1996**). Heavy Metal Toxicity. Retrieved August 2, 2006 retrieved from:
http://www.lef.or g/protocols/prtcl-156.shtml#comm

[7] Kemmer F. M., The Nalco Water Handbook, Mc Graw-Hill, New York pp 13, 14, 18 and

[8] Kenedy J. F., Cabral M. S., Recovery Process for Biological Materials, John Willey & Sons Ltd West Sussex, pp. 369-380, **1993**

[9] Kobranova V. N., Petrophysics, Mir Publishers, Mosco pp 87, **1989**.

[10] Kvech, S., Tull, E., Activated Carbon. Retrieved August 10, **2006**,
from: http://ewr.cee.vt.edu/environmental/teach/wtprimer/carbon/sketcarb.html

[11] Lenntech, H. B.V. Heavy Metals. Retrieved August 8, 2006, from:
http://www.lenntech.com/heavy-metals.htm

[12] Mangun C. L., Braatz R. D., Economy James, and Hall A. J. *Ind. Eng. Chem. Res.* **1999**, *38*, 3499-3504 3499 American Chemical Society Published on Web 08/07/1999

[13] Mark, H. F., Bikales, N. M., Overberger, C. G, Menges, G (Ed), Ecyclopedia of Polymer Science and Engineering, John Willey and Sons, New York, **1988**.

[14] Mohan, D., Singh, K.P., *Water Research*, Vol. 36, No. 9, pp. 2304-2311, **2001**.

[15] Muhammad T., Mamdouh A. A. and Munther I. K., *Journal of Applied Sciences* 5 (3): 482-487, (**2005**)