Post-treatment of Produced water before discharge using *luffa cylindrica*

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Abstract

Sponge-gourds, the fruit of *Luffa cylindrica*, are widely used throughout the world. It is an annual climbing crop which produces fruit containing fibrous vascular system. Produced water is any water that is present in a reservoir with the hydrocarbon resource and is produced to the surface with the crude oil or natural gas. The residual metallic ion concentrations were determined using an Atomic Absorption Spectrophotometer (AAS). The physico-chemical properties of Produced water before discharge or reinjection into the waterways and reservoir and after treatment with *luffa cylindrica* were also determined. The percent removal of metal ions present in the produced water under study were 92.31%, 88.64%, 85.71% and 66.67% for Cr^{3+}, Zn^{2+}, Pb^{2+} and Cd^{2+} respectively. There were also reduction of Sulphate ions, THC, salinity and conductivity. *Luffa cylindrica* is an effective biosorbent for the removal of heavy metal ions; offering a cheap option for primary treatment of produced water.

Keywords

Heavy metal ions; Reservoir; Biosorbent; Reduction; Primary

Introduction

Production of oil and gas is usually accompanied by the production of water. This produced water consists of formation water, or flood water previously injected in the formation. As exploited reservoir mature, the quantity of water produced increases [1]. Produced water is not a single commodity. The physical and chemical properties of produced water vary considerably depending on the geographic location of the field, the geological formation with which the produced water has been in contact for thousands of years, and the type of hydrocarbon product being produced [2].

Most produced waters are more saline than seawater [3]. They may also include chemical additives used in drilling and producing operations and in the oil/water separation process while produced water from gas operations includes condensed water and has higher contents of low molecular-weight aromatic hydrocarbons such as benzene, toluene, ethylbenzene, and xylene (BTEX) than those from oil operations; hence they are relatively more toxic than produced waters from oil production. Studies indicate that the produced waters discharged from gas/condensate platforms are about 10 times more toxic than the produced waters discharged from oil platforms [4].

Imparts of produced water constituents in altering habitat integrity of the natural bodies have been reported in previous studies [5]. It explains that, if untreated produced water is discharge or allowed to accumulate, the decomposition of organic materials it contains can lead to production of large quantities of malodorous gases. All these causes damage to human health, fisheries, and agriculture and results in associated health and economic costs [6]. For these reasons, the immediate treatment and disposal, is not only desirable but also necessary in an industrialized society. This is mandatory by numerous federal and state laws. The ultimate goal of produced water management is the protection of the environment in a manner commensurate with public health, economic, social and political concerns.

OSPAR convention for the protection of the marine environment of the North-East Atlantic requires from the offshore oil industry to develop a “zero discharge strategy” when evaluating the treatment options for produced water [7].

Luffa (*Luffa cylindrica* (L.) Roem syn *L. aegyptiaca* Mill) commonly called sponge gourd, loofa, vegetable sponge, bath sponge or dish cloth gourd, is a member of cucurbitaceous family. The number of species in the genus *Luffa* varies from 5 to 7. Only two species *L. cylindrica* and ribbed or ridge gourd (*L. acutangula* (L.) Roxb) are domesticated. Two wild species are *L. graveolens* and *L. echinata*. *Luffa* is diploid species with 26 chromosomes and a cross-pollinated crop [8].

The fruits of *Luffa cylindrica* are smooth and cylindrical shaped, it is a lignocellulosic material which composed of 60% cellulose, 30% hemicellulose, and 10% lignin [9].

Luffa cylindrica has alternate and palmate leaves comprising petiole. The leaf is 13 and 30 cm in length and width respectively and has the acute-end lobe. It is hairless and has serrated edges. The flower of *Luffa cylindrica* is yellow and blooms on August-September. *Luffa cylindrica* is monoecious and the inflorescence of the male flower is a raceme and one female flower exists. Its fruit, a gourd, is green and has a large cylinder-like shape. The outside of the fruit has vertical lines and a reticulate develops inside of the flesh. *Luffa cylindrica* grows about 12 cm long. The stem is green and pentagonal and grows climbing other physical solid [10].

They have a long history of cultivation in the tropical countries of Asia and Africa. Indo-Burma is reported to be the center of diversity for sponge gourd. The main commercial production countries are China, Korea, India, Japan and Central America [8].

The aim of this study is to use *Luffa cylindrica* as a bioadsorbent to further treat produced water before discharge or reinjection into the waterways and reservoir as the case may be.

Material and Method

Collection of materials

The Produced water sample was collected from oil mining lease (OML) 58, Obagi Flow Station, Total Onshore Operation, in Rivers State, Nigeria at a point before discharge or reinjection (Wash Tank). *Luffa cylindrica* was collected from the bush at Obot Akara in Uyo, Akwa Ibom State, Nigeria.

Preparation of Samples

The sponges-like sample were gathered into a clean bowl and the coat (covering) were removed and put in a furnace at a temperature of 200°C and allowed to dry for 25 minutes. At the expiration of the time, it was removed and cooled in a desiccator for 30 minutes. Finally it was remove and ground to powder.

Experimental Procedures

Produced water collected was stored in corked bottles for immediate analysis in the laboratory. The pH, conductivity, salinity and redox potentials of the produced water samples were measured at the point of sampling using WTW meters. The determination of Zn^{2+}, Cd^{2+}, Cr^{2+}, and Pb^{2+} ions were done using Atomic absorption spectrophotometer (AAS UNICAM 939/959) and sulphate, TOC and THC by the method of AOAC [11].

Adsorption Experiment

5 g of the adsorbent was poured into 50ml of the produced water. The solution was stirred using magnetic pellets for 20 minutes. The separation of the adsorbents and solutions was carried out by filtration with 589^2 Ashless white filter papers and the filtrate stored in sample cans in a refrigerator prior to analysis. The residual of the metallic ion were determined using atomic absorption spectrophotometer (AAS UNICAM 939/959) while THC, TOC, and Sulphate were determined using the procedures stated above.

Results and Discussions

The results of the analysis performed are presented below.

The results of the performance of *luffa cylindrica* in the post treatment of pre-treated Produced water before discharge or reinjection are shown in Table 1. Before the treatment with *luffa cylindrica* it was observed that the pre-treated Produced water on analysis showed that the metal ions present were lower than those obtained with the petroleum industry's BPT (Best Practicable Technology) and BAT (Best Available Technology) (12).

Table 1. Physico-chemical properties of BTWLC and ATWLC Produced water

Parameters	[B]BTWLC Produced Water	[C]ATWLC Produced Water	%Removal	EPA limits
Zn^{2+}(mg/L)	0.044	0.005	88.64	2 – 5
Cd^{2+} (mg/L)	0.003	0.001	66.67	0.03 - 0.1
Cr^{3+} (mg/L)	0.052	0.004	92.31	2
Pb^{2+} (mg/L)	0.007	0.001	85.71	0.1
Sulphate (mg)	72	71.05	1.32	10
THC (mg/L)	13.13	12.17	7.31	42
[A]TOC (mg/L)	78.4	398.4	-	-
[A]pH	7.53	8.69	-	5 – 9
Conductivity (µs/cm)	24.01	23.03	4.08	-
Salinity	14.6	13.9	4.79	-

[A] Table note: Increased after treatment
[B] Table note: Before Treatment with *Luffa Cylindrica*
[c] Table note: After Treatment with *Luffa Cylindrica*

From the results obtained, it was observed that *luffa cylindrica* as an adsorbent was able to further reduce the amount of metal ions present in the pre-treated produced water under study. The percent removal of metal ions present were 92.31%, 88.64%, 85.71% and 66.67% for Cr^{3+}, Zn^{2+}, Pb^{2+} and Cd^{2+} respectively. This could be as a result of adsorption capacity and average BET surface area of fibers of *luffa cylindrica* (13). There were also reduction of Sulphate ions, THC, salinity and conductivity but these reductions were less when compared to that of the metal ions present in the pre-treated produced water under study. The pH and TOC increased after the treatment with *luffa cylindrica* with TOC increasing to a value of 408%. For the pH a close relationship between the surface basicity of the adsorbents and the anions is evident. The increase in TOC may be due to the adsorbent dose of the ground luffa cylindrica under study. This is similar to the findings of others, where the interaction between oxygen-free Lewis basic sites and the free electrons of the anions, as well as the electrostatic interactions between the anions and the protonated sites of the adsorbent are the main adsorption mechanism (14, 15, 16). It was observed that though there was a reduction of sulphate ions present in the produced water after treatment with *luffa cylindrica* (1.32%) the amount of sulphate ions that remained was still above the EPA limit of 10 mg [12], acceptable before discharge or reinjection into the waterways and reservoir respectively.

Conclusions

Growing environmental awareness and stricter regulations are putting exerting demands on industrial produced water. It is not enough to analyzed contaminants; the effluent must meet certain standard of purity before discharge or reinjection into the waterways and reservoir respectively.

This research has also shown that the use of *Luffa cylindrica* as a secondary treatment for produced water is appropriate for the removal of Zn^{2+}, Cr^{3+}, Pb^{2+} and Cd^{2+}. With the high percent removal of metal ions present in the produced water before discharge it showed the potential of *luffa cylindrica* (which is readily available) as an adsorbent for the primary treatment of produced water from the reservoir.

References

1 Cox, R. J., *Subsurface Disposal of Produced Waters: an Alberta Perspective, in Produced Water Technological / Environmental Issues and Solutions*, Proceedings of the International Produced Water Symposium. February 4-7, San Diego, California, USA, 1992.

2 Johnsen S., Frost T.K., Hjelsvold M., Utvik T.R., *The environmental Impact Factor – a proposed tool for produced water impact reduction, management and regulation*, paper 61178 ,Society of Petroleum Engineers, USA, 2000.

3 Cline J.T., *Treatment and discharge of produced water for deep offshore disposal.* Presented at the API Produced Water Management Technical Forum and Exhibition. November 17-18, Lafayette, LA, USA, 1998.

4 Jacobs, R.P.W.M., Grant E., Kwant J., Marqueine J.M., Mentzer E., *The composition of produced water from shell operated oil and gas production in the north sea*. In: J.P. Ray and F.R. Englehart (eds.) Produced Water. Plenum Press, New York, 1992.

5 Ajayi S. O., Osibanjo O., *Pollution Studies on Nigerian Rivers. II. Water Quality of some Nigerian Rivers,* Environ. Pollut., 2: 87-95, 1981.

6 Okpokwasili G. C., Nwabuzor C. N., *Primary biodegradation of anionic surfactants in laundry detergents*, Chemosphere, 17: 2175-2182, 1988.

7 OSPAR, *Strategy on environmental goals and management mechanisms for offshore activities,* Fifth International conference on the protection of the North Sea. www.ospar.org. 11, 2002.

8 Bal K. J., Hari B. K. C., Radha K., Ghale G. M., Bhuwon R.S., Madhusudan P.U., *Descriptors for Sponge Gourd [Luffa cylindrica (L.) Roem.]*, NARC, LIBIRD & IPGRI, 2004.

9 Mazali I.O. Alves O.L., *Morphosynthesis: high fidelity inorganic replica of the fibrous network of loofa sponge (Luffa cylindrica).* Anais da Academia Brasileira de Ciências, Vol. 77, No. 1, p. 25-31, 2005.

10 Lee S., Yoo, J. G. *Method for preparing transformed luffa cylindrica Roem.* World Intellectual Property Organization, (WO/2006/019205), 2006.

11 American Public Health Association, *Standard methods for the examination of water and wastewater* 17th APHA, AWWA, Washington D. C., pp. 1325, 1989.

12 EPA, *Development Document for Effluent Limitations Guidelines and New Source Performance Standards for the Offshore Subcategory of the Oil and Gas Extraction Point Source Category*, EPA 821-R-93-003, U.S. Environmental Protection Agency, 1993.

13 Demir H., Top A., Balköse D., Ulkü S., *Dye adsorption behavior of Luffa cylindrica fibers, J. Hazard Mater*, 153 (1-2):389-94, 2008.

14. Leon Y., Leon C.A., Solar J.M., Calemma V., Radovic L.R., *Evidence for the protonation of basal plane sites on carbon*, Carbon. 30. 797–811, 1992.

15. Radovic L.R., Silva I.F., Ume J.I., Menendez J.A., Leon C.A. , Leon Y., Scaroni A.W., *An experimental and theoretical study of the adsorption of aromatics possessing electron-withdrawing and electron-donating functional groups by chemically modified activated carbons*, Carbon. 35. 1339-48, 1997.

16. Faria P.C.C., Orfao J.J.M., Pereira M.F.R., *Adsorption of anionic and cationic dyes on activated carbons with different surface chemistries.* Water Research, 38, 2043-2052, 2004.