

Treatment of Waste-Water from Pharmaceuticals Industry Using Native Clay

Egbon E.E.¹, Asia, I. O.², Okojie V. U.³, Ize-Iyamu, O.K.⁴,
Idode V. O.⁵, Egbon I. E.⁶

Department of Chemistry, Faculty of Natural Sciences, Ambrose Alli University, Ekpoma, Edo State, Nigeria.

Corresponding author: E-mail: egbon.emmanuel@yahoo.com

ABSTRACT

Waste – water from pharmaceutical plant was collected using composite sampling. This was characterized and treated using native clay samples collected from selected clay deposits in Edo State of Nigeria. The aim was to find out the effectiveness of clay as coagulant in waste water treatment processes. The results of the parameters studied before and after treatment, show significant reduction. For the kaolinite clay, color, Total Solid (TS), Chemical Oxygen Demand (COD), Biochemical Oxygen Demand (BOD), Total Kjeldahl Nitrogen, Phenol and Total Hydrocarbon Count (THC) show percentage reduction of 49.51, 51.89, 73.82, 72.81, 59.24, 82.19 and 33.85 respectively. The mixed clay sample shows percentage reduction of color (35.64), TS (50.57), COD (57.86), BOD (70.70), phenol (80.22) and THC (19.46). Results from this study show that clay material can effectively be used as adsorbent as all the heavy metals were reduced to Below Detectable Level (BDL).

Keywords: Pharmaceutical, waste-water, adsorbent, reduction, composite, native, clay, below detectable level.

INTRODUCTION

There are growing concerns about the pollution of environment by chemicals arising from naturally ecological events and industrial processes which has created the need for new and simple techniques for the treatment of wastewater emanating from such sources. The degradation of the environment due to discharge of pollutants from industrial sources is a real challenge in several countries. This situation is still worse in developing countries where little or no treatment is given before disposal.

Clay minerals are the most vital inorganic components in soil and due to their excellent adsorption properties; they are widely used in environmental applications (Mesomeh, *et al*, 2010, Egbon *et al*, 2011). Clay minerals are effective in adsorbing both organic and inorganic pollutants. This is due to their large specific surface areas and high ion exchange capacity. Understanding of the interaction between pollutants and the surface of the clay is essential for environmental solution design (Belarbi and Al-Malack, 2010).

Waste-water from pharmaceutical industries contains a lot of organic and inorganic constituents potentially harmful to plants and animals. Phenol and allied organic volatile compounds are considered as priority pollutants by world-wide environmental protection agencies like FEPA, USEPA and European Union (EU); and many of them have been classified as hazardous pollutants because of their potential harm to human health (Banat *et al.*, 2000).

Pollution by heavy metals is currently of great concern, due to the increased awareness of the potentially hazardous effects of elevated levels of these materials in the environment. Heavy metals like *Cd (II)*, *Ni (II)*, *Zn (II)* and *Cr (VI)* etc have become prominent pollutants these days due to their toxic and lethal effects. For some time now, increasing amounts of these metals have found their way into the water ways and soil. This higher metal loads in water and soil may increase the up-take by plants and lead to adverse effects on ecosystem and human health. Several methods have been used to treat contaminated water (Gupta and Bhattacharyya, 2006), including use of activated carbon.

Due to the relatively low cost of clay and availability, it easily comes as cheap natural absorbent to remove both organic and inorganic contaminants from wastewater. It plays the role of a natural scavenger by filtering out pollutants from water through both ion exchange and adsorption mechanisms. Clays are hydrous aluminosilicates broadly defined as those minerals that dominantly move up the colloid fraction (<2 μ m) of soil, sediments, rocks and water. The high specific surface area, chemical and mechanical stability, layered structure, high cation exchange capacity, etc, have made the clays excellent adsorbents.

The aim of this work was to investigate the feasibility of using kaolinite and mix-clay in waste water treatment. Laboratory batch process was used to evaluate the adsorption capacity of native clays.

MATERIALS AND METHODS

The waste water samples used were obtained from a pharmaceutical industry located in Edo State. The company specializes in the production of paracetamol (tablets and syrup), quinine, tetracycline, anti-biotic, blood tonic etc.

The different clay samples used for this study were obtained from mid-west part of Nigeria and were used after pre-treatment (Alther, 2004). Basic chemical composition (%) and x-ray diffraction carried out (Egbon 2011). Fig. 1 and 2.

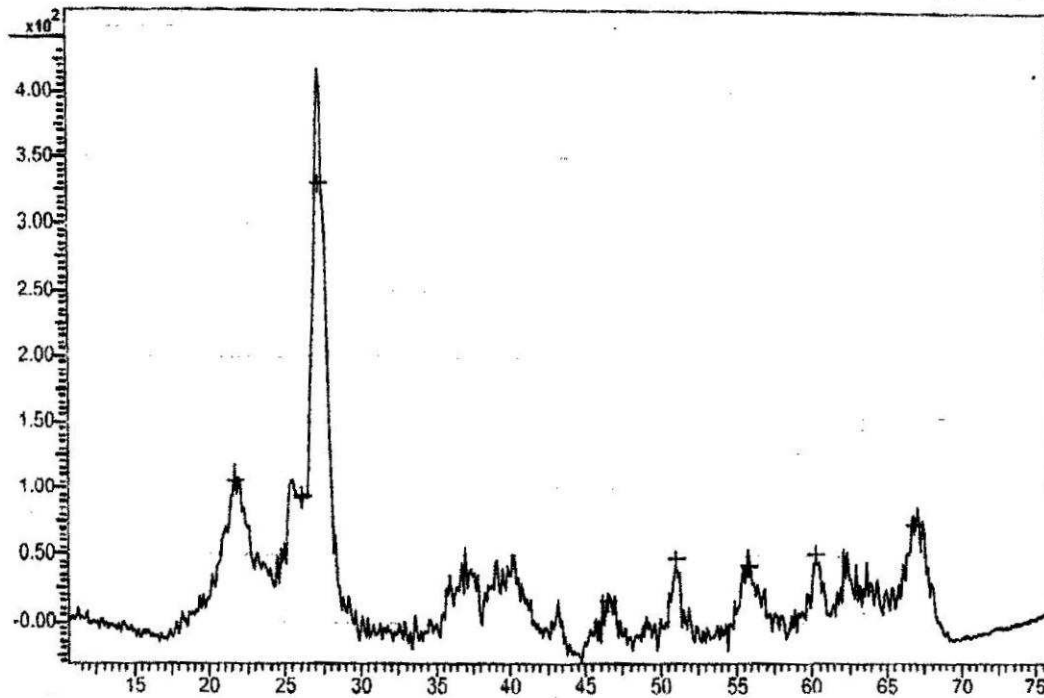


Fig. 1: X-Ray Defraction of Kaolinite Clay Material

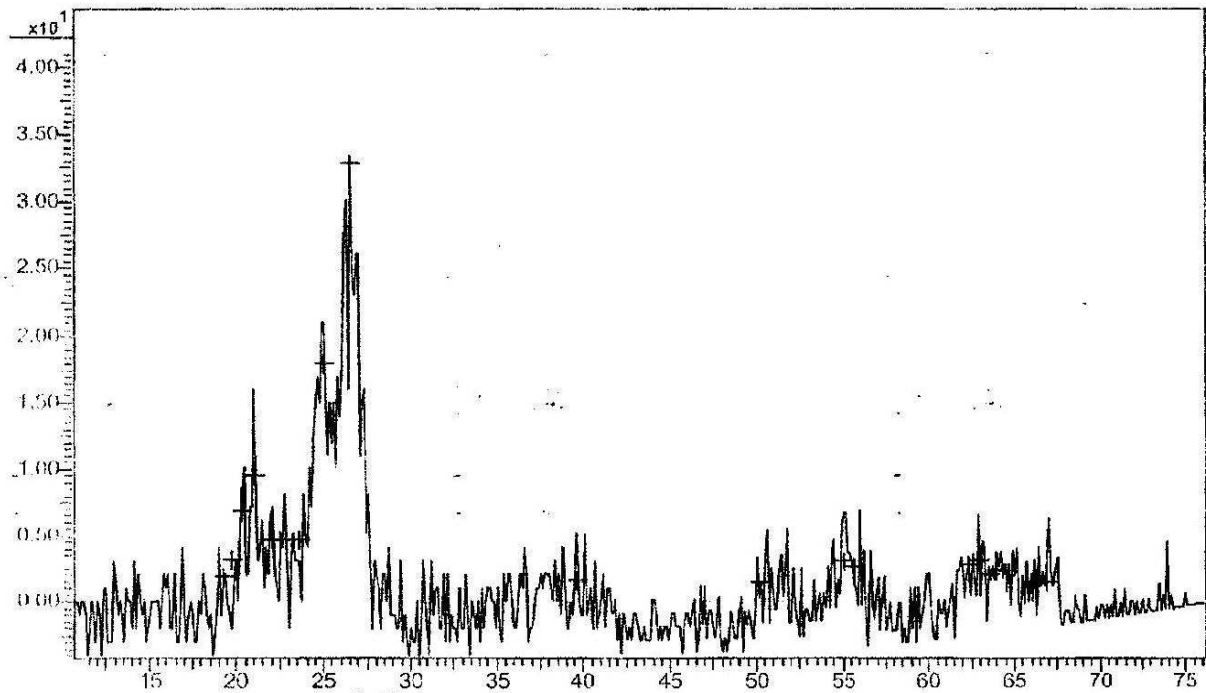


Fig 2: X-Ray Defraction of Mixed Clay Material

The average wastewater generated per day was 2.34×1010^4 litres when production is optimum. The effluent obtained arises from various processes like syrup preparation plasticizers production and tablet rejection.

The effluent is heterogeneous in nature and include water used for washing out processes equipment, breakage of vessels containing the actual preparation, rejected tablets which are crushed and washed down the drain, starch washed from equipment and starch mould and a wide range of chemicals arising from different processing units which are ultimately emptied into the drain.

Representative sample were insured by adequately flushing the service unit line; composite sampling was done by collecting waste water samples on hourly basis for everyday for six days using standard methods for waste-water and effluent analysis (Ademoroti, 1996 and APHA, 2005). The wastewater samples were analyzed before and after treatment with the raw clay materials. The analysis carried on wastewater samples before and after treatment using batch method were pH (using the electrometric method with the aid of a laboratory pH meter, Jenway Model 3150), temperature (using the mercury in glass thermometer) and electrical conductivity (using HACH, TDS conductivity meter. Nitrogen compounds were determined using the Brucine method. Dissolved Oxygen (DO), Chemical Oxygen Demand (COD), Biochemical Oxygen Demand, phenol, total hydrocarbon count (THC) and heavy metals were determined using various method described by Ademori (1996) and APHA (2005) respectively.

The different clay samples used for this study were obtained from the mid-west part of Nigeria and were used after pre-treatment (Alther, 2004). Basic chemical composition (%) and X-ray diffraction carried out (Egbon, 2011). In Fig. 1

RESULTS AND DISCUSSION

Some of the basic chemical composition of the clay samples used is given below in table 1.

Table 1: Chemical composition (%) of the native clay materials:

	pH	CEC Meq/100g)	Surface area (m ² /g)	MgO(%)	CaO (%)	*H ₂ O (%)
Kaolinite A	4.95	72.00	8.09	5.80	6.60	16.10
Illite B	5.41	41.00	9.80	5.75	5/60	11.80
		K ₂ O (%)	Na ₂ O (%)	Fe ₂ O ₃	MnO	
Kaolinite A	1.80		1.61	1.45	0.001	
Illite B	0.01		0.14	3.66	5.75	

* Structural Water

Table 2: Results of untreated and treated pharmaceutical waste water using native clays
 AFTER TREATMENT

Effluent	Effluent	A	Influent	B	Influent
pH	4.90 ± 0.02		7.10 ± 0.30		7.07 ± 0.10
TUR NTU	16.17 ± 0.42		5.00 ± 1.00		4.53 ± 0.34
EC ys/cm	88.27 ± 0.64		5.10 ± 1.00		4.63 ± 8.96
Color pt.co	10.10 ± 0.30		5.10 ± 1.00		6.50 ± 1.74
TS (mg/l)	67.97 ± 0.20		32.70 ± 3.06		33.60 ± 9.50
DO (mg/l)	1.20 ± 0.25		5.33 ± 1.00		5.00 ± 0.82
COD (mg/l)	399.13 ± 1.82		104.50 ± 20.60		168.20 ± 15.0
BOD (mg/l)	147.12 ± 0.13		40.00 ± 2.94		43.10 ± 5.10
NH ₄ ⁺ N (mg/l)	3.87 ± 1.41		1.17 ± 0.29		1.60 ± 0.10
NO ₃ ⁻ N (mg/l)	2.22 ± 0.60		BDL ± 0.00		BDL
TKN (mg/l)	6.87 ± 0.23		2.80 ± 0.15		4.40 ± 0.94
Phenol (mg/l)	4.55 ± 1.18		0.81 ± 0.17		0.90 ± 0.51
THC (mg/l)	2.57 ± 0.37		1.70 ± 0.51		2.07 ± 0.11
Cd (mg/l)	0.03 ± 0.00		BDL		BDL
Cu (mg/l)	0.02 ± 0.00		BDL		BDL
Zn (mg/l)	0.09 ± 0.00		BDL		BDL
Cr (mg/l)	0.016 ± 0.01		BDL		BDL

BDL = Below Detectable level

DO = Dissolved Oxygen

BOD=Biochemical Oxygen Demand

TUR = Turbidity

TS = Total Solids

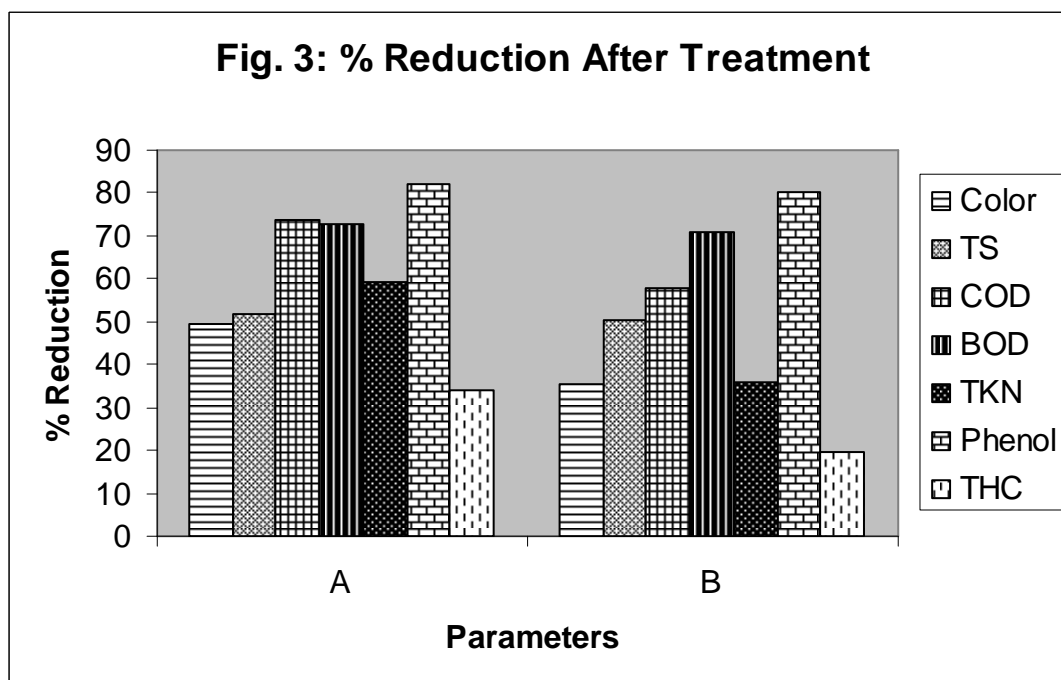
COD=Chemical Oxygen Demand

THC = Total Hydrocarbon Count

TKN = Total Kjeldahl Nitrogen

Percentage (%) Reduction Vs Clay Type (Parameter)

	A	B
Color	49.51	35.64
TS	51.89	50.57
COD	73.82	57.86
BOD	72.81	70.70
TKN	59.24	35.95
Phenol	82.19	80.22
THC	33.85	19.46



The result as showed on table 2 showed that the pH values of the wastewater became slightly alkaline after treatment with clay materials. The relatively high CEC values and structural water of the clay material could be adduced for this and their surface area values (Quirine *et al.*, 2001).

They were noticeable reduction in turbidity and colour after treatment with raw clay materials. The peculiar chemical and mechanical features of clay materials responsible for this could be their swelling ability and scavenging tendencies of clay in water, couple with high their CEC and surface area values. The higher the swelling capacity of the clay, the stronger the barrier it possesses for solid in water and wastewater.

Notably, the reduction of chemical oxygen demand (COD) and biochemical oxygen demand (BOD) of the wastewater by the raw clay samples were exceptionally significant. This could be attributed to the Bronstel – lowry nature of raw clay samples in water (Gupta and Bhattacharyya, 2005) see figure 3 which further suggested that the high level of performance reduction can be due to the presence of some organic pollutants in their ionized form (anionic and cationic) or as neutral molecule. These can be exchanged for the various loosely held ions on the clay mineral surface through ion exchange or inter layer through adsorption mechanism (Egbon *et al.*, 2011).

Raw clay is naturally negatively charged with positively change metal ions on the surface. (Ademoroti, 1996). The high specific surface area, chemical activity in water and mechanical stability, layered structure, high cation exchange capacity etc have made the clays excellent adsorbent materials. Hence, all the heavy metals present in the wastewater were reduced to below detectable level. Various studies have been reported where clays have shown as effective and efficient adsorbents for a large number of inorganic and organic contaminants (Alvarez-Ayuso and Garcia-Sanchez, 2003) based on these properties of raw clays.

CONCLUSION

The potential of clays to adsorb both inorganic and organic contaminants from waste water using batch treatment method was assessed. The results obtained showed the ability of raw clays to reduce turbidity, colour, total solid, COD and BOD, nitrates (nitrogens), phenol, THC etc of waste-water due to their high cation ion exchange

capacities and surface area. Clays can thus be effective when used as coagulant aids for waste water treatment; as all the heavy metal were reduced to below detectable level. The interaction in such cases are often of the ion-exchange type couple with the Fe(III) content of clay materials and the cation exchange capacity of adsorbent materials play a very vital role in this operation as well as surface area.

ACKNOWLEDGEMENT

The authors are grateful to Ambrose Alli University, Ekpoma, Edo State, for providing research facilities for this study and others.

REFERENCES

- Ademorori, C.M.A (1996). Standard Methods for Water and Effluent Analysis. Foludex Press Ltd, Ibadan.
- Alther, G.R. (2004). "Some Practical Observation on the Use of Bentonite" *Environment and Engineering Geoscience*. **(4)**: 347-359
- Alvarez-Ayuso, E. and Garcia-Sanchez, A. (2003). Clays, Clay Minerals. **51**:4475
- APHA, AWWA, WPCF (2005). "Standard Methods for the Examination of Water and Waste-water. 23rd Edition. *American Public Health Association*, Washington D.C.
- Banat, F. A., Al-BAshir, B., Al-Saheh, S. and Hei Yajneh, O. (2000). Adsorption of Phenol by Bentonite. *Environmental pollution* **107**:391-398
- Belarbi, H. and Ali-Malack, M.H. (2010). Adsorption and Stabilization of Phenol by Modified Local Clay. *International Journal of Environmental Research*, **4**(4): 855-860
- Egbon, E.E., Ebhoaye, J. E., Asia, I. O., Ize-Iyamu, O.K., Egbon I. E. and Ehigbor, M. J. (2011). Treatment of Waste-water from Food Industry Using Clay. *ChemTech Journal*, Vol. **7**: pp.19 – 23
- Masomeh, S.M., Saeed B., Morteza, T. and Ali N. (2010). Adsorption of Petroleum Hydrocarbons on Organoclay. *Journal of Applied Chemical Researches*. Vol. 4, No. 14: 19 – 23
- Quirine, K., Shao, R. and Renuke, R. (2001). "Estimating Cation Exchange Capacity" from Cornell Soil Test Data nmsp.css.cornel.edu/publication/factsheet.ets.esp.factsheet.series. **22**: 322-325

ACKNOWLEDGEMENT

We specially acknowledge the Ambrose Alli University, Ekpoma for the provision of the laboratory used in carrying out this work.

This academic article was published by The International Institute for Science, Technology and Education (IISTE). The IISTE is a pioneer in the Open Access Publishing service based in the U.S. and Europe. The aim of the institute is Accelerating Global Knowledge Sharing.

More information about the publisher can be found in the IISTE's homepage:

<http://www.iiste.org>

CALL FOR JOURNAL PAPERS

The IISTE is currently hosting more than 30 peer-reviewed academic journals and collaborating with academic institutions around the world. There's no deadline for submission. **Prospective authors of IISTE journals can find the submission instruction on the following page:** <http://www.iiste.org/journals/> The IISTE editorial team promises to review and publish all the qualified submissions in a **fast** manner. All the journals articles are available online to the readers all over the world without financial, legal, or technical barriers other than those inseparable from gaining access to the internet itself. Printed version of the journals is also available upon request of readers and authors.

MORE RESOURCES

Book publication information: <http://www.iiste.org/book/>

Recent conferences: <http://www.iiste.org/conference/>

IISTE Knowledge Sharing Partners

EBSCO, Index Copernicus, Ulrich's Periodicals Directory, JournalTOCS, PKP Open Archives Harvester, Bielefeld Academic Search Engine, Elektronische Zeitschriftenbibliothek EZB, Open J-Gate, OCLC WorldCat, Universe Digital Library, NewJour, Google Scholar

