

Equilibrium and Thermodynamic Consideration of Cd^{2+} , Ni^{2+} and Pb^{2+} Removal From Aqueous Solution Onto Treated and Untreated *Cola Nitida* Waste Biomass

F. U. Okwunodulu¹, N. O. Eddy²

¹Department of Chemistry, Michael Okpara University of Agriculture Umudike, Nigeria

²Department of Chemistry, University of Zaria, Nigeria

Abstract: Adsorption principles and techniques are used in the treatment of effluent water from industries and other sources. The use of adsorbent such as *Cola nitida* husk has been recommended as one of the ways of reducing the concentrations of heavy metals in wastewater. In this study, the influence of pH and temperature on the adsorption of Cd^{2+} , Ni^{2+} and Pb^{2+} onto unmodified and modified *Cola nitida* waste was investigated. The result showed that Cd^{2+} , Ni^{2+} and Pb^{2+} exhibited maximum adsorption of 99.99 mg/g by unmodified *Cola nitida* husk at pH of 2-10 for Cd^{2+} ; pH of 2, 4, 8 and 10 for Ni^{2+} ; pH of 2, 6, 8 and 10 for Pb^{2+} while 99.78 mg/g Cd^{2+} , 99.51 mg/g Ni^{2+} at pH 6 and 99.67 mg/g Pb^{2+} at pH of 2 was achieved by modified *Cola nitida* husk. 99.96 mg/g Cd^{2+} , 99.99 mg/g Ni^{2+} and 99.92 mg/g Pb^{2+} at 303K (30 °C) was also achieved by unmodified *Cola nitida* husk while 99.92 mg/g Cd^{2+} , 99.64 mg/g Ni^{2+} and 98.90 mg/g Pb^{2+} at 303K (30 °C) was equally achieved by modified *Cola nitida* husk. The values of E_a , ΔS_{ads}^0 , ΔH_{ads}^0 and ΔG_{ads}^0 gotten showed that the adsorption process is by physical adsorption, spontaneous, feasible and exergonic (release of free energy), endothermic and occur with increasing degree of orderliness.

Keywords: Adsorption, metal removal, temperature, pH, *Cola nitida* husk.

1. Introduction

The tremendous increase in the effluents discharge is one of the most important environmental challenges which need to be addressed. Heavy metals rank as major pollutant in industrial wastewater [1]. According to [2], [3], cadmium and lead are mutagenic and carcinogenic even at very low concentrations. Asthmatic condition has also been documented for inhalation exposure to nickel [4], while acute inhalation exposure may produce headache, nausea, respiratory disorders and death [5], [6].

The application of conventional methods of cadmium, nickel and lead removal such as electro dialysis, ultrafiltration, ion-exchange, reverse osmosis, flocculation, crystallization, chemical oxidation or reduction etc are often restricted due to their technical or economical constraints [7], [8]. Much had been reported on the use of waste biomass as a natural adsorbent in heavy metal removal from industrial waster [9], [10], [11], [12], [13], [14], [15], [16], [17] and many others. This research investigated the use of *Cola nitida* husk as an adsorbent in the removal of Cd^{2+} , Ni^{2+} and Pb^{2+} from their aqueous solutions. *Cola nitida* husk is a waste generated from processing the seed. Considerable quantities of this waste suitable for use as livestock feed components are lost or underutilized. [18] reported that Nigeria produced 2 million metric tons of *Cola nitida* annually which represented 70% of world *Cola nitida* production and its waste generated. Moreover, the presence of anti-nutritional factors such as theobromine, caffeine and tannin could possible reduce nutrient digestibility at high levels [19] hence, its use is limited and larger waste generated. However its proximate composition [20] classified it as a cellulosic material, its tannin composition classified it as a

celluloses material and its tannin composition also classified it as a good adsorbent for a wide range of solutes particularly bivalent metal cations [21]. Therefore the utilization of this waste will minimize environmental pollution and equally manage its waste. In this research, the influence of pH and temperature on Cd^{2+} , Ni^{2+} and Pb^{2+} removal from aqueous solution by adsorption onto unmodified and modified *Cola nitida* husk was investigated.

2. Materials and Methods

The *Cola nitida* was obtained from Gariki Market Okigwe in Imo State and processed to get the husk. The husk was grounded into tiny particle size using manual grinder and sieved through a test-sieve shaker after washing with de-ionized water and drying in oven at 50 °C for 12hrs to get 250 μm mesh size. It was then activated by soaking in 2% (v/v) dilute nitric acid solution for 24 hours, filtered, rinsed severally with de-ionized water and allowed to dry in the oven at 105 °C for about 6 hours. Hence labeled unmodified sample. About 10 g portion of the activated sample was modified using mercarptoacetic acid by soaking the sample into 1000 cm^3 of 0.3 mol mercarptoacetic acid for 2hrs at 25 °C, filtered, rinsed with de-ionized water and finally dried at 50 °C for 12hrs. 100 mg/l concentration of Cd^{2+} , Ni^{2+} and Pb^{2+} prepared as an aliquot from the stock solution of 1000 mg/l was used. To determine the effect of pH on Cd^{2+} , Ni^{2+} and Pb^{2+} adsorption from their aqueous solutions, 50 m^3 portions of the metal ion solutions of 100 mg/l were introduced into various 250 ml flask containing 1 g of both unmodified and modified samples after varying the metal ion solutions with 0.1M HCl for low pH and 0.1M NaOH for higher pH in order to obtain pH ranges of 2, 4, 6, 8 and 10 respectively at 25 °C. After 1 hr, the solution mixtures

were filtered, and the final metal ion concentrations in the filtrate were determined by AAS (Buck model 200A). Moreover, to determine the effect of temperature on the metal ions adsorption from aqueous solutions, experiment was performed in a constant speed shaking water bath and the effect of these temperature variations [303 K (30 °C) 323 K (50 °C), 342 K (70 °C), 363 K (90 °C) and 383 K (110 °C)] on adsorption were investigated. The same pH experimental procedure was repeated on temperature at pH of 7.5.

3. Results and Discussion

Effect of pH on Cd²⁺, Ni²⁺ and Pb²⁺ adsorption by unmodified and modified *Cola nitida* husk: Concentrations of metal ions adsorbed by unmodified and modified *cola nitida* husk at various pH and at 298k are presented in Table 1 as shown below.

Table 1: Concentrations of Cd²⁺, Ni²⁺ and Pb²⁺ adsorbed by *Cola nitida* husk from aqueous solutions at various pH and at 298 K.

pH	Unmodified <i>Cola nitida</i> husk			Modified <i>Cola nitida</i> husk		
	Cd ²⁺ (mg/g)	Ni ²⁺ (mg/g)	Pb ²⁺ (mg/g)	Cd ²⁺ (mg/g)	Ni ²⁺ (mg/g)	Pb ²⁺ (mg/g)
2	99.994 ± 0.001	99.999 ± 0.012	99.989 ± 0.006	98.936 ± 0.060	96.720 ± 0.952	99.672 ± 5.138
4	99.996 ± 0.000	99.989 ± 0.007	99.899 ± 0.035	98.896 ± 0.078	99.452 ± 0.370	86.660 ± 1.937
6	99.998 ± 0.000	99.876 ± 0.043	99.998 ± 0.010	99.784 ± 0.319	99.514 ± 0.398	89.300 ± 1.692
8	99.998 ± 0.000	99.999 ± 0.012	99.999 ± 0.010	98.952 ± 0.053	98.866 ± 0.108	86.660 ± 1.937
10	99.998 ± 0.000	99.999 ± 0.012	99.998 ± 0.010	98.780 ± 0.130	98.570 ± 0.024	92.668 ± 0.750

Both unmodified and modified *Cola nitida* husk exhibited good adsorption capacity on the metal ions though unmodified one had slightly higher adsorption capacity than the modified one. Maximum values for the unmodified sample were given as 99.99 mg/g Cd²⁺ at pH of 2 - 10, 99.99 mg/g Ni²⁺ at pH of 2, 8, 10 and 99.99 mg/l Pb²⁺ at pH of 2, 6, 8 and 10 while modified *Cola nitida* husk achieved its maximum of 99.78 mg/g Cd²⁺, 99.51 mg/g Ni²⁺ at pH of 6 and 99.67 mg/g Pb²⁺ at pH of 2. It was obvious that maximum values were obtained at both low and high pH. Increased adsorption at low pH may be due to increased protonation (H⁺) by the neutralization of the negative charges at the surface of the biosorbent which facilitates diffusion process and provides more active sites of the biosorbent [22] while increased adsorption at high pH shows the precipitation of the soluble metal ions with increased functional group on the cell wall due to deprotonation of the metal binding sites, which promotes the metal uptake [23].

Effect of temperature on Cd²⁺, Ni²⁺ and Pb²⁺ adsorption by both unmodified and modified *Cola nitida* husk: The amount of Cd²⁺, Ni²⁺ and Pb²⁺ adsorbed by unmodified and modified *Cola nitida* husk at initial concentration of 100 mg/l after 1hr in variation with temperature (K) is shown in Table 2.

Table 2: Concentrations of Cd²⁺, Ni²⁺ and Pb²⁺ adsorbed by *Cola nitida* husk from aqueous solutions at various temperatures

T (K)	Unmodified <i>Cola nitida</i> husk			Modified <i>Cola nitida</i> husk		
	Cd ²⁺ (mg/g)	Ni ²⁺ (mg/g)	Pb ²⁺ (mg/g)	Cd ²⁺ (mg/g)	Ni ²⁺ (mg/g)	Pb ²⁺ (mg/g)
303	99.963 ± 0.069	99.999 ± 0.013	99.923 ± 0.027	99.920 ± 0.165	99.636 ± 0.150	98.896 ± 1.407
323	99.927 ± 0.053	99.979 ± 0.004	99.887 ± 0.111	99.952 ± 0.179	99.212 ± 0.040	96.074 ± 0.145
343	99.905 ± 0.043	99.975 ± 0.002	99.853 ± 0.004	99.624 ± 0.032	99.320 ± 0.009	96.016 ± 0.119
363	99.795 ± 0.006	99.963 ± 0.004	99.841 ± 0.009	99.544 ± 0.004	99.224 ± 0.034	94.715 ± 0.463
383	99.457 ± 0.158	99.939 ± 0.014	99.807 ± 0.025	98.720 ± 0.371	99.110 ± 0.085	93.048 ± 1.208

It was observed that the extent of adsorption decreased with increase in temperature and with modification, indicating that the adsorption of these heavy metal ions by the *Cola nitida* husk favours the mechanism of physical adsorption. Arrhenius equation (1) was used to study the effect of temperature on the amount of heavy metal ions adsorbed.

$$\log k = \log A - \frac{E_a}{2.303RT} \quad (1)$$

where k is the rate constant for the adsorption process, A is the pre-exponential factor, E_a is the activation energy for the adsorption process, R is the gas constant and T is the temperature. From equation 1, a plot of log k versus 1/T should be linear with slope equal to E_a/2.303R and intercept equal to log A. Fig. 1 shows the Arrhenius plots for the adsorption of Cd²⁺, Ni²⁺ and Pb²⁺ by unmodified and modified *Cola nitida* husk

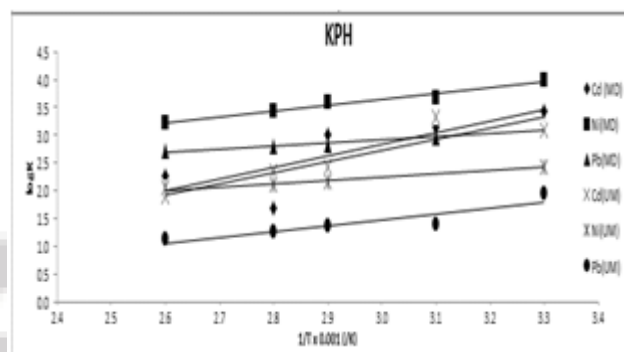


Figure 1: Variation of log k with 1/T for the adsorption of Cd²⁺, Ni²⁺ and Pb²⁺ by unmodified and modified *Cola nitida* husk

Table 3: Transition state parameters for the adsorption of Cd²⁺, Ni²⁺ and Pb²⁺ by unmodified and modified *Cola nitida* husk

system	Ions	Slope	LogA	E _a (J/mol)	A	R ²
<i>Cola nitida</i> husk	Cd(MD)	2.0913	-3.4402	39.11	0.0003	0.7247
	Ni(MD)	1.0656	0.4523	19.93	2.9663	0.9689
	Pb(MD)	0.5626	1.2265	10.52	0.0524	0.9706
	Cd(UM)	1.9863	-3.2267	37.14	0.0004	0.8403
	Ni(UM)	0.5769	0.5159	10.79	3.4564	0.9727
	Pb(UM)	1.0653	-1.7115	19.92	0.0163	0.8302

Parameters deduced from the plots are presented in Table 3. From the results obtained, R^2 values ranged from 0.72 to 0.97 indicating an excellent degree of fitness of the adsorption data to the Arrhenius model; E_a values ranged from 10.52 to 37.14 J/mol indicating that the values are within the range of values expected for the mechanism of physical adsorption. Enthalpy and entropy changes for the adsorption of metal ions by unmodified and modified *Cola nitida* husk was estimated using the transition state equation (2) [24].

$$\log \frac{k}{T} = \log \frac{R}{Nh} + \frac{\Delta S_{ads}^0}{2.303R} - \frac{\Delta H_{ads}^0}{2.303RT} \quad (2)$$

Where k is the adsorption rate constant, T is the temperature, R is the gas constant, N is the Avogadro's number, h is the plank constant, ΔS_{ads}^0 and ΔH_{ads}^0 are the standard entropy and enthalpy changes for the adsorption process. Fig. 2 shows the transition state plot for the adsorption of Cd^{2+} , Ni^{2+} and Pb^{2+} by unmodified and modified *Cola nitida* husk.

Figure 2: Variation of $\log(k/T)$ with $1/T$ for the adsorption of Cd^{2+} , Ni^{2+} and Pb^{2+} by unmodified and modified *Cola nitida* husk

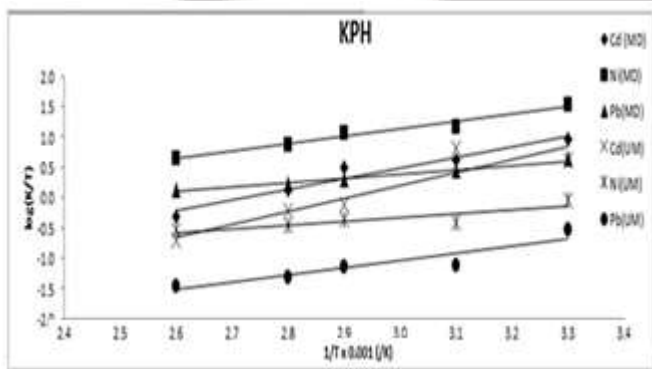


Table 4: Transition state parameters for the adsorption of Cd^{2+} , Ni^{2+} and Pb^{2+} by unmodified and modified *Cola nitida* husk

System	Ions	Slope	Intercept	ΔH^0 (J/mol)	ΔS^0 (J/mol)	R^2
Cola nitida husk	Cd(MD)	1.7598	-4.7996	33.70	-417.59	0.9507
	Ni(MD)	1.2138	-2.5171	23.24	-373.89	0.9746
	Pb(MD)	0.7125	-1.7125	13.64	-358.48	0.9829
	Cd(UM)	2.1332	-6.1927	40.84	-444.27	0.8588
	Ni(UM)	0.6138	-2.167	11.75	-367.18	0.7748
	Pb(UM)	1.2147	-4.6845	23.26	-415.39	0.8639

Thermodynamic parameters deduced from the plots are presented in Table 4. From the results obtained, it can be seen that ΔS_{ads}^0 values are negative indicating that the adsorption of the studied ions occurs in a state of orderliness while the positive values obtained for ΔH_{ads}^0 indicate that the adsorption process is endothermic. Also the Gibb's free energy (ΔG^0) was calculated from equation (2), (3) and (4) [25]

$$(\Delta G^0 = -RT \ln K) \quad (3)$$

$$\ln k = \frac{\Delta S_{ads}^0}{2.303R} - \frac{\Delta H_{ads}^0}{2.303RT} \quad (4)$$

where $\frac{\Delta S_{ads}^0}{2.303R}$ is equals to intercept and

$$\frac{\Delta H_{ads}^0}{2.303RT}$$

is equals to slope

The values obtained from Table 5 shows that the ΔG^0 values for the adsorption of these metal ions is negative indicating that the adsorption process is spontaneous, feasible and exergonic (release of free energy) [26]

Table 5: The Gibb's free energy (ΔG^0) for metal ions adsorption onto *Cola nitida* husk at initial concentration of 100 mg/l in variation with temperature (K).

Temp. (K)	Unmodified			Modified		
	Cd^{2+}	Ni^{2+}	Pb^{2+}	Cd^{2+}	Ni^{2+}	Pb^{2+}
303	-146979	-114816	-132910	-13674	-120332	-112752
323	-156681	-122394	-141684	-10845	-145767	-120195
342	-166382	-129973	-150457	-11517	-154792	-127637
363	-176084	-137552	-158677	-12189	-163818	-135080
383	-185786	-145130	-168003	-12860	-172844	-142522

4. Conclusion

Treatment of industrial effluents before discharge should be adopted. In this work, the use of unmodified and modified *Cola nitida* husk of 250 μm particle size was used in the adsorption of Cd^{2+} , Ni^{2+} and Pb^{2+} from their aqueous solutions. The effect of pH and temperature were investigated. The result obtained showed that unmodified *Cola nitida* husk had a better performance than the modified one hence could be an effective adsorbent for the removal of metal ions from aqueous solutions

5. Recommendations

- (1) Adsorption studies should be carried out on *Cola nitida* husk in order to determine its adsorption capacity on other toxic heavy metals and metalloids like Hg, As, Cu, Cr etc.
- (2) Pretreatment and modification effect on *Cola nitida* husk is crucial as to determine their effect on adsorption capacity of this adsorbent.
- (3) Considering recent developments in environmental quality standards there is need for treatment of metal-bearing effluents before discharge in order to maintain free environmental pollution. Moreover, the utilization of this waste will minimize environmental pollution and equally manage this waste. As a waste management, they can be effectively utilized in the detoxification of heavy metal ions from aqueous solution system

6. Future Scope

The impact of this study to the society involves the use of low cost adsorbents in maintaining pollution free environment since it involves waste management and detoxification of toxic pollutants. Moreover this study gives an insight for the upcoming researchers to adopt this method in different research areas such as in agricultural research i.e. a situation where this adsorbent will be mixed with fertilizers before application in order to minimize its leaching to the environment.

Reference

[1] E. Valdman, L. Erijman, F. L. P. Pessoa, S. G. F. Leite, "Continuous biosorption of Cu and Zn by immobilized

- waste biomass *Sargassum sp.*," Process Biochemistry, XXXVI, pp. 869 – 873, 2001.
- [2,4,5] R. Goyer, "Toxic effects of metals In: Casarett and Doull's Toxicology," 4th ed. Amidur, M. O., Doull, J. D and Klaassen, C. D. eds. Pergamon Press, New York. pp. 623 – 680, 1991.
- [3] M. Kumar, D. P. S. Rathore, A. K. Sing, "Amberlite XAD-2 functionlized with o-aminophenol: synthesis and applications as extractant for Cu(II), Co(II), Cd(II), Ni(II), Zn(II) and Pb(II)," Atlanta LI, pp. 1187 – 1196 (2000).
- [6] R. E. G. Rendall, J. I. Philips, K. A. Renton, "Death following exposure to fine particulate nickel from a metal" Arc. Process Ann. Occup. Hyg, pp. 921 – 930, 1994.
- [7] S. Bossrez, J. Remade, J. Goyette, "Adsorption of nickel by *Enterococcus hirae* cell walls," Journal of chemical technol. and biotechnol XC (1), pp. 45 – 50, 1997.
- [8] Q. Yu, P. Kaewsarn, "Binary adsorption of copper(II) and cadmium(II) from aqueous solutions by biomass of marine algae *Durvillaea potatorum*" Separation Science and Technology, XXXIV (8), pp. 1595 – 1605, (1999).
- [9] S. S. Montes, G. E. Valero, S. L. Morales, A. M. Vilches, R. Schmidt, "Adsorption capacity of copper of natural and modified radiata bark pine," J. of the Chilean Chem. Society, VIII (4), pp. 124-128 (2003).
- [10] H. Mahri, D. Naghipour, F. Vaezi, S. Nazmara, "Teawaste as an adsorbent for heavy metal removal from industrial wastewaters," American J. of Applied Sci., II (1), pp. 372-375, 2005.
- [11] M. A. Hanafiah-Megat, S. C. Ibrahim, M. Z. Yahaya, "Equilibrium adsorption study of lead onto sodium hydroxide modified Lalang (*Imperata cylinrica*) leaf powder," Plant soil environ. L (6), pp. 257-264, 2006.
- [12] J. C. Igwe, M. N. Ekeghe, A. A. Abia, "Binding of Hg^{2+} , Ni^{2+} and Pb^{2+} ions from aqueous solutions onto thiolated and carboxymethylated sawdust," Int .J. of Chem., XVI (3), pp. 121-128, 2006.
- [13] E. E. Akporhonor, P. A. Egwaikhide, "Removal of selected metal ions from aqueous solution by adsorption onto chemically modified maize cobs," International Journal of Applied Env. Sci., II(2), pp. 93-94, 2007.
- [14] N. Das, D. Charumanthi, R. Vimala, "Effect of pretreatment of Cd^{2+} biosorption by mycehial biomass of *Pleurotus florida*," African Journal of Biotechnology, VI (22), pp. 2555-2558, 2007.
- [15] S. M. I. Sajidu, I. Persson, W. R. L. Masamba, E. M. Henry, "Mechanisms for biosorption of Chromium(III), Copper(II) and Mercury(II) using water extract of *Moringa oleifera* seed powder. Africa Journal of Biotechnol. VII (6), pp. 800-804, 2008.
- [16] T. M. Ansari, K. Umbreen, R. Nadeem M. A. Hanif, "*Polypogon monspeliensis* waste biomass: a potential biosorbent for Cd(II), African Journal of Biotech., VIII (6), pp. 1136-1142, 2009.
- [17] G. O. Agiri, O. Akaranta, "Adsorption of Metal Ions by Dye Treated Cassava Mesocarp," Scientific Research and Essay, IV(5), pp. 526-530, 2009.
- [18] J. A. Oluokun, E. A. Olalokun, "The effects of graded levels of brewers spent grains and kolanut pod meal on the performance characteristics and carcass quality of rabbits," Nigerian Journal of Animal Production, XXVI, 71-77, 1999.
- [19] E. C. Bate-Smith, "Phytochemistry of tannis: the concept of relative astringency," Phytochemistry, XII pp. 907-912, 1973.
- [20] Oladayo, "Proximate composition of some agricultural wastes in Nigeria and their potential use in activated carbon production," J. Appl. Sc. Environ. Manage., XIV (1), pp. 55-58, 2010.
- [21] J. A. Laszlo, F. R. Dintzis, "Crop residues as ion-exchange materials treatment of soybean hull and sugar beet fibre (pulp) with epichlorohydrin to improve cation exchange capacity and physical stability," Journal of applied polymer science, LII, pp. 521 – 528, 1994.
- [22,27] A. Mittal, L. Kurup, J. Mittal, "Freundlich and Langmuir adsorption isotherms and kinetics for the removal of tartrazine from aqueous solutions using hen feathers. Journal of Hazardous Materials, CXLVI (1-2), pp. 243 – 248, 2007.
- [23,28] Y. Sag, D. Ozer, T. Kutsal, "A comparative study of the biosorption of Pb(II) ions to *Z. ramigera* and *R. arrhizu*," Process Biochemistry, XXX (2), pp. 169 – 174, 1995.
- [24] Y. A. Yahaya, M. M. Don, S. Bhatia, "Biosorption of Cu(II) ions onto immobilized cells of Pycnoporos sanguineus from aqueous solution: Equilibrium and kinetic studies, Journal of Harzadous Materials, CLXI, 189 – 195, 2009.
- [25] Y. S. Ho, "Removal of copper ions from aqueous solution by tree fern, Water Research, XXXVII, pp. 2323 – 2330, 2003.
- [26] A. F. Onuchukwu, "Chemical thermodynamics for science students," 3rd ed. Academic Publishers Owerri-Nigeria XXXVI, pp. 137-142, 1996.

Author Profile

F. U. Okwunodulu has done B.Sc. in Pure Chemistry from University of Nigeria Nsukka and M.Sc. and Ph.D in Environmental Chemistry from Michael Okpara University of Ariculture Umudike, Nigeria. Currently an academic staff of Michael Okpara University of Ariculture Umudike, Nigeria.

N. O. Eddy has done B.Sc. in Chemistry from University of Calabar, Nigeria and M.Sc. in Environmental Chemistry from Michael Okpara University of Ariculture Umudike, Nigeria.

N. O. Eddy has done Ph.D in Physical Chemistry from University of Calabar, Nigeria. Currently working as Professor of academics in University of Zaria, Nigeria.