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Enhancing Nitrate Reduction in Palm Oil Factory Wastewater Using Cost Effective Activated Natural Clay Adsorbent

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ABSTRACT

High level of nitrates from palm oil mill wastewater causes pollution in the environment. The reduction in its content was done using natural and activated Kaolin clay. The aim of this research is to use local abundant and low cost adsorbent in the reduction of nitrates. Mineral logical composition of clay was done using X-ray diffractometer, standard methods America Public Health Association (APHA) standard was used UV-Visible spectrophotometer with a percolating media containing clay stone in ratio 3:1. The nitrate level in palm oil effluent 55.70mg/L after treatment it was reduced to 5.31mg/L for natural Kaolin and 3.4mg/L for activated kaolin. Based on World Health Organization (WHO) standard it is high enough to cause pollution. It was shown that kaolin has the capacity to reduce nitrates from palm oil mill wastewater when activated kaolin has greater capacity for nitrate removal than natural kaolin.

1.0 INTRODUCTION

The most widely produced vegetable oil in recent times is palm oil. It is used in food and as energy source due to its high content of saturated and unsaturated fats [1]. In areas where if is in abundance, it is highly valuable for its production in terms of economy as a major source of livelihood for the inhabitants, creating jobs directly and indirectly. However, despite the inherent advantages, palm oil production is also associated with some environmental problems such as loss of tropical forest, carbon emissions, declining biodiversity, etc. [2]. During processing of palm oil, a lot of water in needed, and about 50-89% of wastewater effluent accompanying the processing activity is of no economical value, and requires complex treatment. As a result, it is being discharged into the environment (Amelia, et al, 2017). Processing mills located close to surface water bodies' discharge their effluents directly into them without meeting specific effluent quality standard [3]. Liquid waste generated from palm oil, first the fresh bunch as a processed by steam sterilization with pressure of about 2.5kg $1cm^3$ at 140-above. This produces wastewater drain from each of the sterilizer (drums).

Nutrients in palm oil wastewater include nitrogen, phosphorus, potassium, magnesium and calcium, all of which are essential components of organic fertilizer [4]. The nutrients in palm oil mill effluent can thus act as soil ameliorant to restore fertility on marginal soils. Nitrogen is an essential plant nutrient needed for growth, development and reproduction critical compound of organic molecules as proteins, amino acids, and nucleic acid, the key point in photosynthesis [5]. It is found as nitrates to be readily utilized by plants in the form of.(NO_3^- and NH_4^+). ATP – Adenosine triphosphate is an energy carrying molecule found in cells of all living things. ATP captures chemical energy obtained from breakdown of food molecules and releases it to fuel other cell processes. It serves as shuttle delivering energy to places within cell where energy consuming activities are taking place. Excess nitrate level in streams can damage water quality [6], cause eutrophication and pose health risk to animals and humans. It is a component of ATP that is required for the transfer of energy in plants. However, an excess nitrate level in streams can damage water quality [6], cause eutrophication and pose health risk to animals and humans. On the other hand, its deficiency is one of the most important factors limiting crop production worldwide [7]. In a bid to limit the inherently excessive level of nitrates in effluents accompanying palm oil production, there is the need for some form of pre-treatment prior to discharge into the environment [8].

Clays are raw materials for reduction of pollutants. Natural Kaolin clays and bentonites are potential low-cost adsorbent for nitrate removal from palm oil effluent. Kaolin clays are used as adsorbent of its high surface area that can hold onto others molecules or particles. Its unique structures provide numerous sites for adsorption to take place, making it suitable for purifying water. Adsorption is one of the methods which can reduce pollutants. . Adsorption involves a substance been adsorbed on to the surface of an adsorbent [9]. Zeolite and Bentonites have been shown to have more superior properties due to their colloidal particles and high ion surface capacity and their uses have been carried out [10]. The use of kaolin clays in adsorption of pollutants have been carried out in the desalination of seawater and other pollutants such as NO_3^{2-}, Pb^{2+}, Cl^-, biochemical Oxygen Demand (BOD), Chemical Oxygen Demand (COD) and reduction of bacteria count [11]. Agbor is the largest miller of palm oil and home of kaolin.
In this research, Kaolin clay is used as an alternative material, since it is in large quantities in the area. However its utilization is not on a large scale. This paper describes the use of kaolin clays to reduce nitrates in wastewater from palm oil mill to industrial activities to reduce management of the environment at low cost.

2. Materials and Methods

2.1 Study Area
Ozanagog is located in AgborIka South Local Government Area of Delta State with GPS coordinates of 6^0 15^0 50.73120N and 6^0 $12^0$6.7788^{0}E. Zanagogo is $6^0 8^1$-$6^0$10N Latitude and Longitude $6^0 6^1$-$6^0 17^1$E.

Map of Agbor

2.1.1 **Sample collection**
Natural Kaolin clay was crush with chisel and distilled water added 150 ml. About 60 g of it was used, thoroughly mixed together and sieved using a 100Nm mesh. Wastewater samples were collected from aerobic periods on hourly basis for one month and stored in ice container and taken to the laboratory.

Small stones were collected from the river bank at Ogbasogba River leading to Ota after Agbor Technical College in Ika South Local Government Area.

2.2 Kaolin Activation
60g of natural Kaolin clay was soaked in 150/mL of 1.5HCLm, stirred at 150 rpm for 1 hour on a magnetic stirrer. The mixture was filtered and washed with distilled water. The residue was then heated to 200^0 C for about an hour. It was stored in a desiccator to dry. This is the activation process.
Effluents from oil mills carefully collected in 50 liters clean plastic containers with time and days varied, this was used to constitute constant pressure head and having a top at the bottom to control flow of wastewater from mill. Plastic column of height 100cm and diameter 10cm were set up for both natural and activated kaolin clays. Glass wool was carefully packed to a depth of 5cm into its base. Quantities of mixed clay and stones in ratio 3:1 were carefully loaded into the vat to 70cm mark.

2.3 Analysis of Palm Oil Mill Waste Water
Elemental analysis and Mineralogical analysis for the different clay types present was done using X-ray diffractometer (XRD, model Phillips PW-1800). Geochemical analysis using Atomic Absorption spectrophotometer (model HACH 2010), while nitrogen determination was done using standard methods [12] and using UV-visible spectrophotometer spectral 10, Hatch model Co. Ltd Tokyo standard solutions of nitrates were made of different dilutions from stock solution and measured at the appropriate wavelengths and pH done on site using auto mated sensor PH meter 08 model.

3. Result and Discussion

3.1 Kaolinite Activation
Activation of Kaolin was carried out by treating with HCl, the Cations that are present in the Kaolin with H^+ thereby releasing Al^3, Fe^{3+} and Mg^{2+} from it. This help to increase the sites which have become active with the addition of HCl thereby increase the ratio. When these sites become active, the activity of the clay increases. HCl also help in removing impurities and rearrange the ions for cation exchange capacity. Some studies uses activated bentonite clay for hours or an hour and oven-dried at 200^0c [13]. In this study suggest kaolin clay with drying period of an hour and it is low cost. For kaolin clay at low pH,
$(Al^{3+})_2(0^2)_{3(3)} + 6H^+ = 2Al^{3+}_{(99)} + 3H_20(aq)$-(I) | $(AL_4)(Si_8)0_20$ (04) $4+6H^+ =(Al_2)(Si_8)0_20(OH)_2+2Al^{3+}+ 4H_20^{(-1)}$ When activation takes place, there is cationic exchange of salts like Mg^{2+} and Ca^{2+} with the hydrogen H^+ formed from the acid, resulting in dissolution of Al^{3+} and other ions from kaolin lattice layer. The release of Al^{3+} and other ions from kaolin lattice layer. The release of Al^{3+} is shown in above equation (1)
Characterization of kaolin clay of natural and acid activation is shown in figures 1 and 2. In the natural kaolin, the peaks are jointed together without distinct

peaks, whereas after activation the peaks were clearly separated and sharp showing peaks for different minerals separated.

Table 1: Mineral characterization of clay Kaolin (%)

Clay Minerals	Natural	Activated
Smectite group	Nil	5.8
Montrinorillonite	8.2	10.21
Chloride	Nil	10.04
Illite	12.4	6.17
Interstratified	15.42	21.40
Kaolinite	39.37	30.25
Quartz	24.50	10.00

From the Table 1 above we have natural kaolin having montmorillonite, illite, interstratified kaolin and Quartz, while that activated showed all the components of smectite, montmorillonite, chloride, illite, interstratified, kaolinite and quartz [14]. Clay samples containing montmorillonite are mixtures of other minerals containing $Al_20_3.4si.H_20$ including Mg and Ca. Although they are kaolin clays because it was activated, they can be expanding water retention capacity with high, cation exchange capacity.

Table 2: Geochemical Analysis of Kaolin clay %

Metal oxide%	Natural	Activated
SiO_2	44.44	43.37
Al_2O_3	38.50	35.80
Fe_2O_3	9.20	7.67
Na_2O	0.83	0.86
MgO	0.67	1.82
K_2O	1.06	1.68
TiO_2	0.80	1.98
CaO	-	2.00

Table 2 shows the geochemical analysis of natural and activated clay (Kaolin). They are mostly dominated by silica SiO_2 and Al_2O_3 meaning they are aluminosilicate clays. It is more prominent in natural clay.

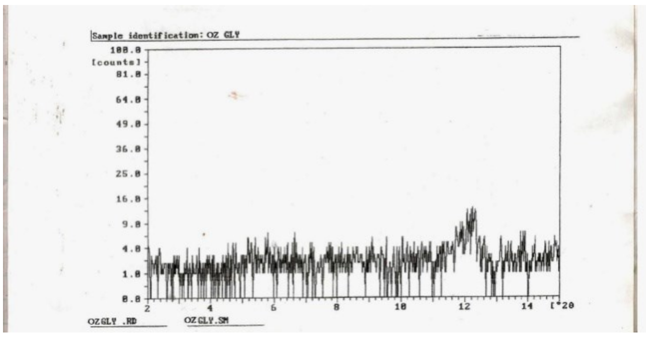

Figure 2:

Analysis of nitrate was done by using standard nitrate solution of varying concentrations 0.5mgN/L, 1.0mgN/L, 1.5mg/L, 2.0mg/L and 2.5 mg/L at an absorbance of 220-240nm and the calibration absorbent curve shown in Fig 3 in accordance with Beer-Lambert's Law A= a,b,c where absorbance is directly on proportional to concentration.

Table 3: Results of Nitrate and pH Analysis of palm oil Mill Effluent.

Parameters	Raw Value(mgLe)	Natural Kaolin	Activated Kaolin
Nitrate	55.70	5.31	3.41

The above result shows that the load of nitrate is high from the palm oil mill and when channeled directly into the river has the ability to cause algae growth, which can ultimately result in eutrophication. This can reduce the amount of dissolved oxygen in the water body. Similar study have shown that aerobic process can reduce pH, COD, BOD, TDS, total nitrogen and nutrient solution [15]. Figure 3 shows nitrogen absorbance versus concentration. Activated Kaolin have better absorption capacity than natural Kaolin given it bigger hole pores and active sites with HCl acting as activator [13]. This is an indication that local Kaolin clay can reduce nitrate from waste water mill oil.

Table 4: Result of Contact Time Mean Values

Time to obtain first drop $1h^{-1}$	2.1	4hrs.01mins
Time to $1h^{-1}$ obtain 100ml	3hrs slm	6hrs.23mins

Table 4 shows the residence time to obtain the first drop and 100ml of water from the palm oil waste. This depends on the clay mineralogy. Kaolin clays do not expand only when they have other components in them. After activation with HCL, it will possess some swelling capacity which may be responsible for the time of collection which is known as the residence time. It is also the time for the absorbate to interact directly. If the liquid phase containing the adsorbent is stationary, the adsorbate diffuses through the adsorbate surface is due slowly. In both activated and natural kaolin clays, the amount of nitrate absorbed is due to the time contact between nitrate ions and the active sites on the clay [16]. It is to be noted that the kaolin is capable of lowering nitrate levels in palm oil mill waste. HCl is used to effect activation since the mineral acid can dissolve the Al_2O_3 and SiO_2 which are the pores component of the clay. This is in accordance [17], this also open up the pores on the surface areas that were closed, which results in greater absorption capacity.

Kaolin has both positive and negative charges, it negative charges tends to repel pollutants like nitrate, but with the presence of Fe and Al ions on the surface of the clay will tend to react with molecules of water in the nitrate solution. This is done by capturing ions H^+ of hydrogen or OH^- release on hydration thereby becoming positively charged by the presence of H^+ and Al^{3+}.

$H_2O.A^-+M+Clay=M^+-Clay.A^-+H_2O$ ……………… (3)

Where A^+ could be OH, Cl NO_3. It could also be attributed to the anionic nature of clay and it is repelled from the surface and explained by their theory that clays possess OH groups which when exposed to external species like aluminum and silicon are liable given rise to positively charged clay in anionic exchanged as show in equation 3 so as to bind the negatively charged nitrates. Besides kaolin clays, bentonites, biochar, seashells can be used in treating industrial waste with other pollution parameters [18] after pyrolysis between 400-600^{0}C. Also chitosan, bentonite and activated carbon were used to reduce residual oil and suspended solids [15]. The major advantage of using HCl for activation is that it reduces free acid in waste oil palm which is helpful in environmental damage caused by industrial activities [19].

Conclusion

From the study, it has been observed that Kaolin clay is a potential raw material for reduction of nitrates in palm oil mill waste. There are natural and activated clays that are readily available, low-cost adsorbent with good percentage reduction. Reduction of nitrates by kaolin clay depends on the mineral composition. The presence of smectite and montmonuonite clays which are expanding clay influenced the reduction of pollutant nitrate from oil mill wastewater. This work will help make use of natural abundant material (Kaolin Clay) in the proffering solution to environment issues.

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