

# The Role of Ripe *Musa sapientum* (Plantain) Peels in the Removal of Phosphorus and Nitrogen from Aqueous Solution

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## Abstract

The effluents that are generated from wastewaters are major contributors to various water pollution problems. The aim of this study was to investigate the applicability and feasibility of using plantain peel in the removal of phosphorus and nitrogen in aqueous solutions, using four different modifications of the peel at three (2.5%, 5 % and 10 %) different concentrations. Although some measure of phosphate absorptions were observed in the presence of some of the peel medications, remarkable nitrate removals were observed in the presence of all the peel modifications used. In the presence of the untreated carbonated sample, after a 5 h contact period, nitrate levels were shown to decrease from the initial concentration of 297.80 mg/L to 174.46 mg/L, 196.57 mg/L and 221.91 mg/L, at 2.5 %, 5 % and 10 % peel concentrations, respectively. Nitrate levels after a 5 h contact time in the presence of the treated carbonated peel revealed a decrease from 297.80 mg/L to 144.21 mg/L, 174.33 mg/L and to 202.10 mg/L, at 2.5 % 5 % and 10 % peel concentrations, respectively. Also, after a 5 h contact time, nitrate levels in the aqueous solution in the presence of the treated raw peel were observed to change from an initial level of 297.80 mg/L to 280.60 mg/L, 164.58 mg/L and 151.98 mg/L, at peel concentrations of 2.5 %, 5 % and 10 %, respectively. The study was able to reveal the potential of using this agro-waste for use in the bioremediation of polluted wastewater effluents.

**Keywords:** Nitrogen, phosphorus, plantain peels, wastewater

## 1. Introduction

The effluents that are generated from wastewaters are major contributors to various water pollution problems. Some of these problems are eutrophication, which can stimulate the growth of algae, increased water purification cost, interference with the recreational value of water, health risks to humans and livestock, excessive loss of oxygen and undesirable changes in aquatic populations (Akpor and Muchie, 2011). Water pollution as a result of phosphorus and nitrogen compounds has been a major source of eutrophication, hence a concern for environmentalists and environmental engineers. Also, several damages to the quality of receiving water, is due to effluent discharges from industrial and domestic wastewaters (Surchi, 2011).

In recent years, there is greater environmental awareness on the need to treat wastewater effluents before discharging into receiving water bodies. This has necessitated a great deal of research into finding cost-effective methods for the removal of contaminants from wastewater (Zahra, 2012).

The conventional practices in the removal of nutrient from polluted waters are chemical and biological. Because of the high capital and operational costs which may be associated with the generation of secondary waste which present treatment problems, such as volume of sludge produced during chemical treatment, the method is not advocated in recent years (Kumar, 2006). Despite the advantages (low capital and operating costs, reduction of aquatic toxicity and operations take place at ambient temperature) of biological nutrient removal, there are still a host of drawbacks. The disadvantages include: some chemical compounds do not readily degrade by biological treatment and biocides used in the manufacturing environment greatly inhibit biological reactions. In addition, the digestion rates are slow, hence, requiring large storage tanks. For the microbes not to die off during treatment; there must also be an enabling environment and available nutrients for their survival (Roman, 2000; Schultz, 2005).

There have been reports on new approaches based on the use of natural adsorbents that are inexpensive for treatments. It is generally reported that an adsorbent is termed as low cost if it requires little processing and is abundant in nature or is a by-product or waste from another industry (Nasim *et al.*, 2004; Badmus *et al.*, 2007; Surchi, 2011). In addition, it is argued that since agricultural products and by-products are abundant waste materials that need proper disposal other than burning, which can generate carbon dioxide and other forms of pollution, the conversion of these products into useful and hopeful value-added products, of which nutrient removal is one, is an environmental friendly decision (Kumar, 2006).

In order to obtain treatment processes that are cost effective and efficient, there is a need to explore the feasibility of using indigenous agro-waste for the removal of nutrients from polluted waters. Although in recent

years, several natural products, usually considered waste, such as sugar cane bagasse, peanut shells, banana peels, coconut shell and apple waste, have been reported to be used in the extraction of pollutants from water (Namasivayam and Sangeetha, 2005; Castro *et al.*, 2011), there is the paucity of information on the role of plantain peels in the removal of these eutrophic nutrients from water. This study was therefore aimed at investigating the applicability and feasibility of using plantain peel in the removal of phosphorus and nitrogen in aqueous solutions, using different modifications of the peel.

## 2. Materials and Methods

The ripe plantain peels used for the study were obtained from the local market in Omu-Aran, Kwara State, Nigeria. The plantain peels were cleaned in deionised water to remove sand and other debris. The cleaned peels were oven-dried at 50 °C for 5 d, after which they were pulverized into fine powder using a sterilized food mill. The pulverized powder was stored in air-tight plastic containers at room temperature until use or further treatment.

For this investigation, four different forms of the pulverized peels were used. The forms were the raw pulverized peel, which did not undergo any form of further treatment after drying, araw pulverized peels which were treated with 20 % sulphuric acid, carbonated peels that was not subjected to any form of treatment, and carbonated peels that were treated with 20 % sulphuric acid. For carbonation, approximately 250 g of the pulverized peel was placed in a crucible and placed in an oven at a temperature of 300 °C for 1 h.

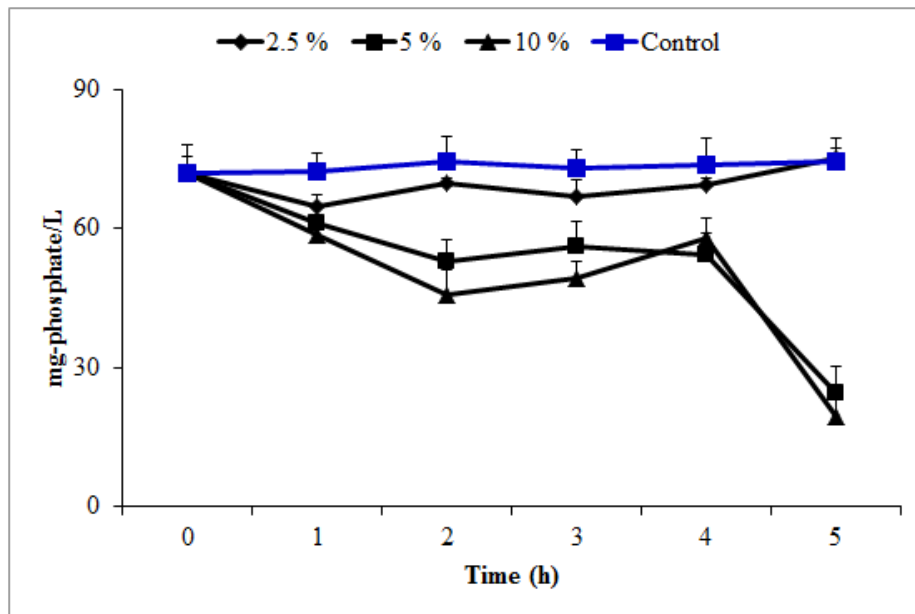
For treatment, to a 50 g of the raw or carbonated peel in a 250 mL beaker, 100 mL of 20 % sulphuric acid was added. The content was allowed to react for 1 h, with stirring every 5 min to obtain a homogenous mixture. At the expiration of the 1 h treatment period, the content was diluted and washed several times with deionised water and filtered through Whatman No 1 filter paper. The aim of the washing was to make sure that every trace of the acid is removed. This was confirmed by testing with a litmus paper. Where it was confirmed through the litmus paper that a trace of acid was still present, the filtrate was further washed in deionised water and re-filtered. After filtration, the supernatant was dried in a hot air oven at 80 °C for 24 h. In this paper, the four categories of peels used for the investigation were referred to as follows: untreated raw peel, treated raw peel, untreated carbonated peel, and treated carbonated peel.

Nutrient removal studies, using the different peel types were carried out as follows: To a 100 mL Erlenmeyer flask, containing 40 mL of deionised water that was spiked with known quantities of potassium nitrate and potassium dihydrogen phosphate, to serve as nitrate and phosphate sources, respectively, a known quantity of the respective categories of the plantain peels were added and placed in a rotary shaker, at a shaking speed of 100 rpm throughout the period of the study. Prior to the start of the experiment, the initial concentration of phosphate and nitrate was analysed. This is to ascertain the concentrations of these nutrients at time 0 h. After the addition of the respective peel types to the flask containing the aqueous solution, on an hourly basis, for the next 5 h, the contents of each respective flask was filtered through Whatman No 1 filter paper. The filtrate was then determined for phosphate and nitrate concentrations, using standard methods (APHA, 2001). Phosphate was determined using the ascorbic acid method while nitrate was determined using the salicylate method. All analyses and designs were carried out in triplicates. Also, all reagents used for the investigation were of analytical grades.

Statistical analyses were carried out using the PAST: Paleontological statistics software package for education and data analysis, as described by Hammer *et al.* (2001). The test for comparison of means was done using the One-Way Analysis of Variance (ANOVA) while test of relationship was carried out using the Pearson Correlation Index. All statistics were carried out at 95 % confidence interval.

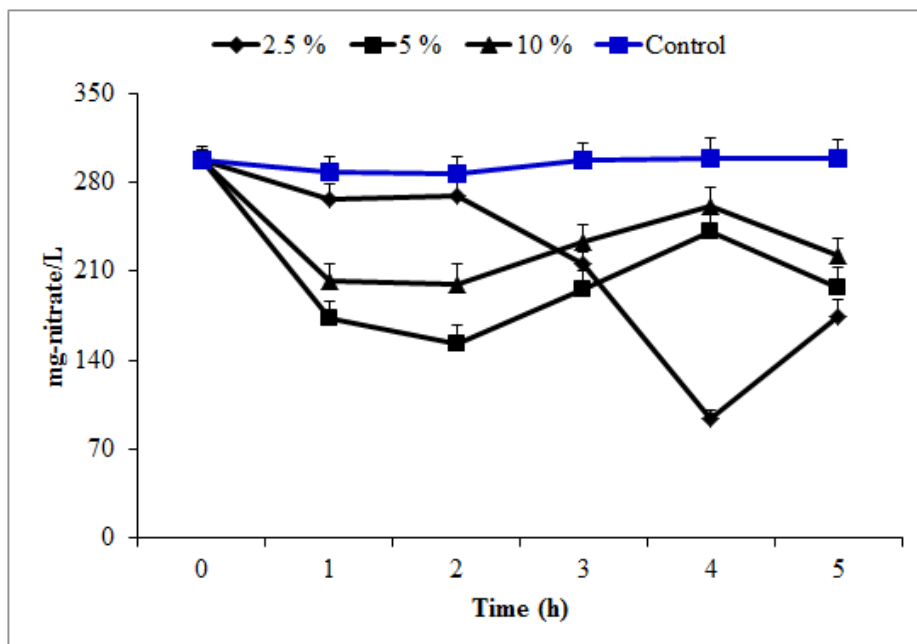
## 3. Results

When in contact with the untreated carbonated plantain peel, phosphate levels in the aqueous solution was not observed to follow any pattern with time at 2.5 % peel concentration. After a 5 h contact time, phosphate levels increased from 71.79 mg/L to 75.15 mg/L. At higher peel concentration of 5 % and 10 %, there were significant decreases in phosphate concentration with time. At the end of the 5 h contact period, phosphate levels decreased from 71.79 mg/L to 24.46 mg/L, at 5 % peel concentration and from 71.79 to 19.62 mg/L, at 10 % peel concentration (Fig. 1). At the end of the 5 h contact time, phosphate levels at peel concentrations of 5 % and 10 % were observed to be significantly lower than levels at 2.5 % peel concentration ( $p \leq 0.05$ ).



**Fig. 1: Changes in phosphate concentration in the aqueous solution containing different concentrations of the untreated carbonated plantain peel**

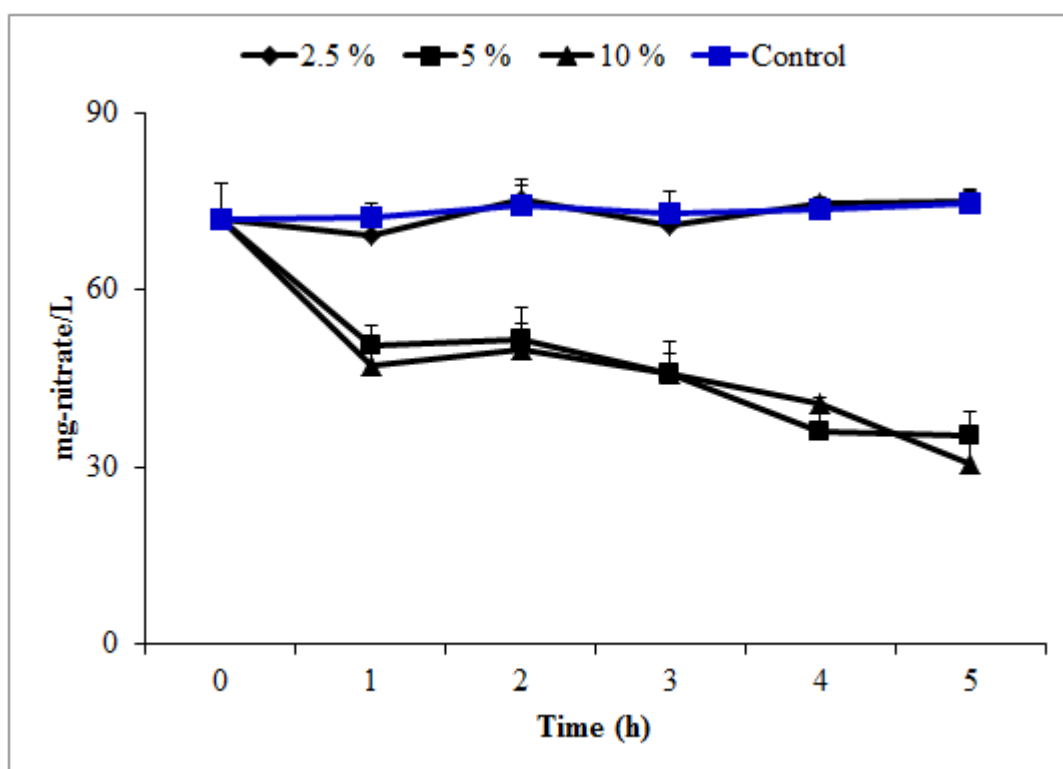
In the case of nitrate in the presence of the untreated carbonated sample, at peel concentration of 2.5 % in the aqueous solution, a significant decrease in concentration was observed after 4 h contact time, decreasing from 297.80 mg/L at 0 h to 93.47 mg/L. At peel concentrations of 5 % and 10 %, slight decreases in concentration were only observed at 2 h contact period, after which there were consistent increases with time. At the end of the 5 h contact period, nitrate levels were shown to decrease from the initial concentration of 297.80 mg/L to 174.46 mg/L, 196.57 mg/L and 221.91 mg/L, at 2.5 %, 5 % and 10 % peel concentrations, respectively (Fig. 2). When compared with the control, nitrate levels in the aqueous solution containing the respective peel concentrations were observed to be significantly lower ( $p \leq 0.05$ ). This trend was irrespective of the peel concentration used.



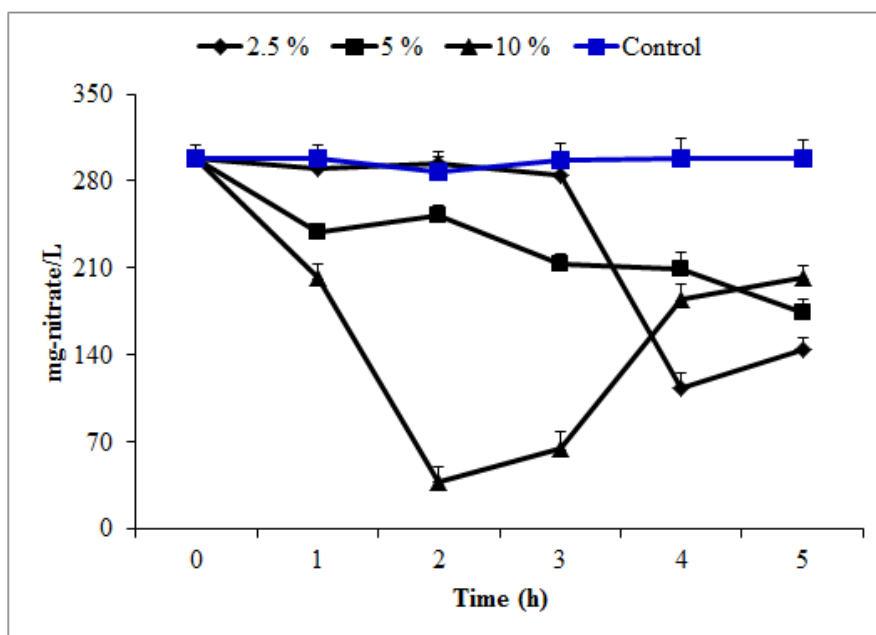
**Fig. 2: Changes in nitrate concentration in the aqueous solution containing different concentrations of the untreated carbonated plantain peel**

In the treated peel samples, phosphate levels were observed to decrease significantly at the end of the 5 h contact time, at peel concentrations of 5 % and 10 %. At a peel concentration of 2.5 %, phosphate levels did not follow any particular trend with contact time. There were slight decreases and increases with contact time. At the end of the 5 h contact time, phosphate levels were found to have increased from 71.79 mg/L to 74.80 mg/L, for peel concentration of 2.5 %. At peel concentrations of 5 % and 10 %, phosphate levels decreased to 33.32 mg/L and 30.68 mg/L, respectively, at the end of the 5 h contact time and at intermittent (Fig. 3). The concentrations of phosphate at 5 % and 10 % peel concentrations were observed to be significantly lower than concentration of the control and at 2.5 % peel concentration ( $p \leq 0.05$ ).

In the presence of the treated carbonated peel, nitrate levels in the aqueous solution at peel concentration of 2.5 % was observed to decrease from 297.80 mg/L to 144.21 mg/L, after 5 h contact time. At that peel concentration, minimum nitrate level of 113.84 mg/L was observed after 4 h contact time. For peel concentrations of 5 % and 10 %, minimum nitrate levels of 52.23mg/L and 38.63 mg/L, respectively were observed at 2 h contact time, after which there were consistent increases. At the end of the 5 h contact period with the peels, nitrate levels were shown to decrease from 297.80 mg/L to 174.33 mg/L and to 202.10 mg/L, at 5 % and 10 % peel concentration, respectively (Fig. 4). After the 5 h incubation time, nitrate level at peel concentration of 10 % was observed to be significantly higher than at 2.5 % and 5 % peel concentrations ( $p \leq 0.05$ ).

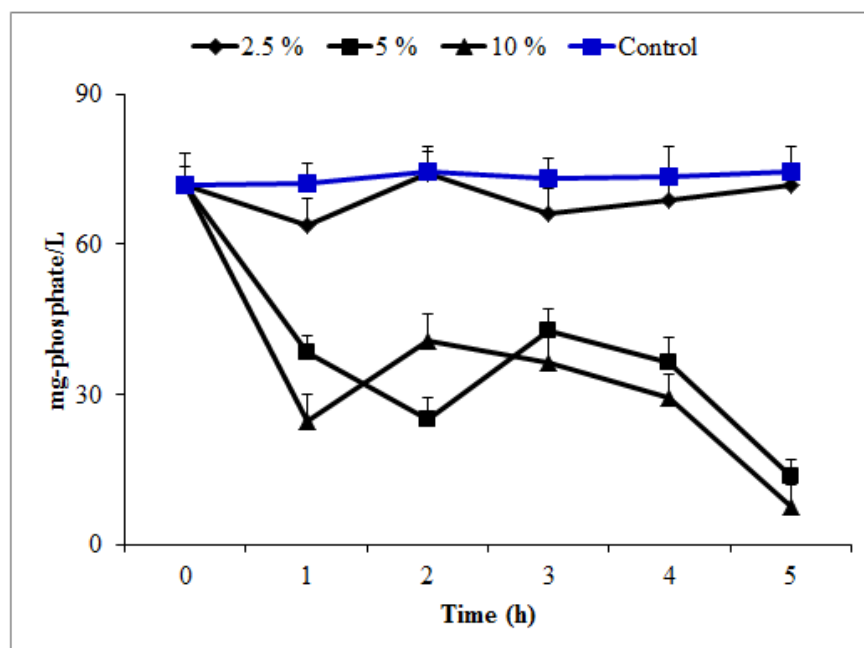


**Fig. 3: Changes in phosphate concentration in the aqueous solution containing different concentrations of the treated carbonated plantain peel**



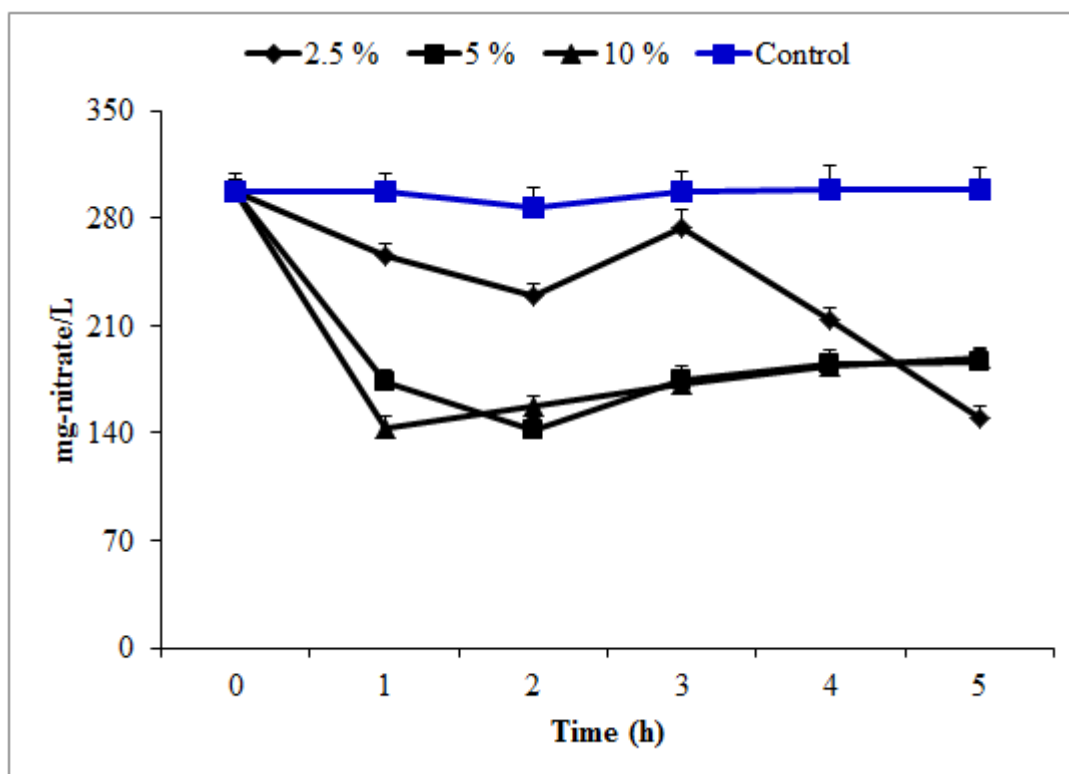
**Fig. 4: Changes in nitrate concentration in the aqueous solution containing different concentrations of the treated carbonated plantain peel**

As in Fig. 5, in the presence of the untreated raw peel, phosphate concentrations were observed to decrease from 71.79 mg/L to 71.64 mg/L, 13.64 mg/L and 7.71 mg/L, in the presence of peel concentrations of 2.5 %, 5 % and 10 %, respectively. At peel concentrations of 5 % and 10 %, significant decreases in phosphate concentration were already observed after 1 h contact period. At peel concentration of 2.5 %, no significant change in phosphate concentration was observed with contact time (Fig. 5). The phosphate levels at peel concentrations of 5 % and 10 % were observed to be significantly lower than those in the control and peel concentration of 2.5 % ( $p \leq 0.05$ ).



**Fig. 5: Changes in phosphate concentration in the aqueous solution containing different concentrations of the untreated raw plantain peel**

For nitrate concentration in the presence of the untreated raw peel, minimum level of 149.99 mg/L was observed after 5 h contact period at 2.5 % peel concentration. At peel concentrations of 5 %, minimum nitrate level of 142.04 mg/L was observed after 2 h contact time while a minimum level of 143.10 mg/L was observed after 1 h contact time (Fig. 6). Generally, after 5 h contact period the concentrations of nitrate at the different peel concentrations were observed to be significantly lower than that of the control ( $p \leq 0.05$ ). This trend was irrespective of the peel concentration used.



**Fig. 6: Changes in nitrate concentration in the aqueous solution containing different concentrations of the untreated raw plantain peel**

In the case of the treated raw peel, no remarkable phosphate removal was observed at peel concentration of 2.5 %. At peel concentrations of 5 % and 10 %, significant decreases in phosphate levels were observed after 1 h contact period and were observed throughout the 5 h period. At the end of the 5 h contact period, phosphate levels were found to change from 71.79 mg/L to 74.85 mg/L, from 71.79 mg/L to 23.57 mg/L and from 71.79 mg/L to 21.64 mg/L, at peel concentrations of 2.5 %, 5 % and 10 % concentrations, respectively (Fig. 7). After the expiration of the 5 h contact period, phosphate levels at 2.5 % peel concentration and the control were observed to be significantly higher than peel concentrations at 5 % and 10 % ( $p \leq 0.05$ ).

For nitrate concentrations in the treated raw peel, significant decrease to 133.09 mg/L was observed after 2 h contact period, at peel concentration of 2.5 %, after which there were significant increases with time. At peel concentration of 5 % and 10 %, significant decreases in nitrate level to 97.88 mg/L and 111.98 mg/L, respectively were observed after 1 h contact period. At the end of 5 h contact period, nitrate levels were observed to change from an initial level of 297.80 mg/L to 280.60 mg/L, 164.58 mg/L and 151.98 mg/L, at 2.5 %, 5 % and 10 % peel concentrations, respectively (Fig. 8). After the 5 h contact time, nitrate levels at the different peel concentrations, were observed to be significantly lower than that of the control ( $p \leq 0.05$ ).

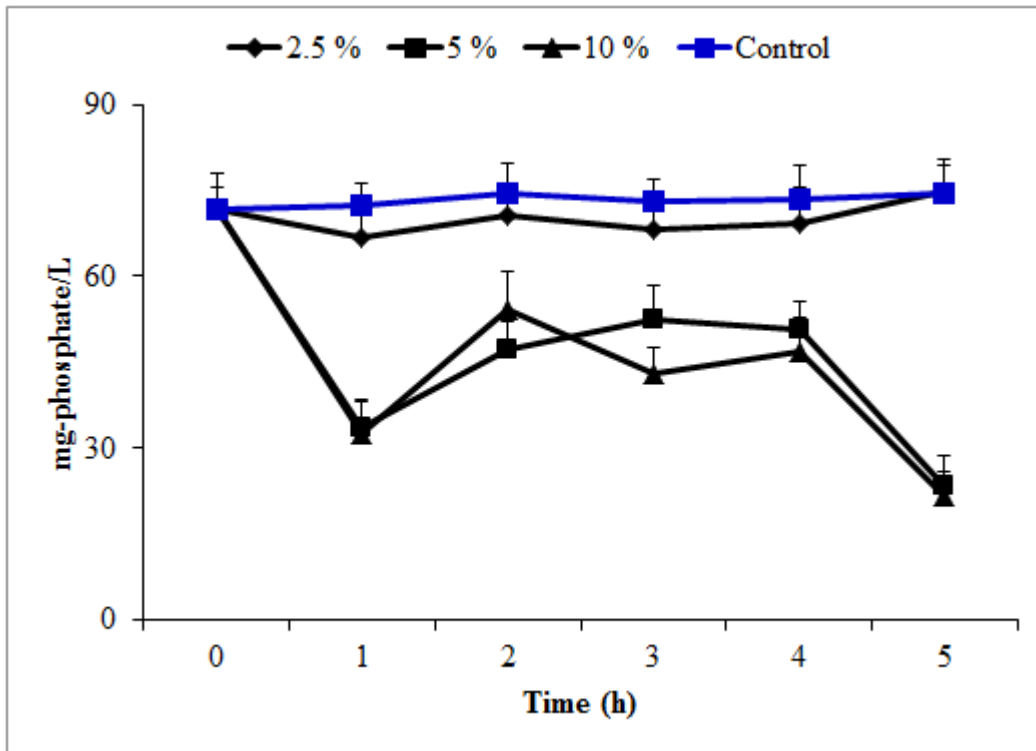


Fig. 7: Changes in phosphate concentration in the aqueous solution containing different concentrations of the treated raw plantain peel

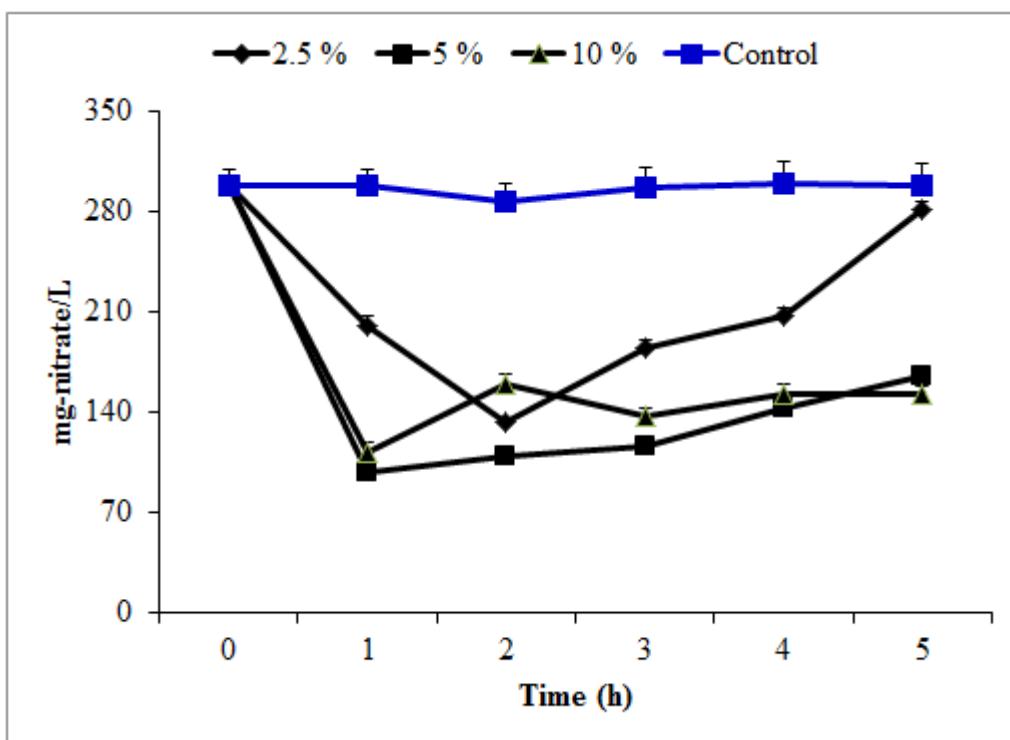
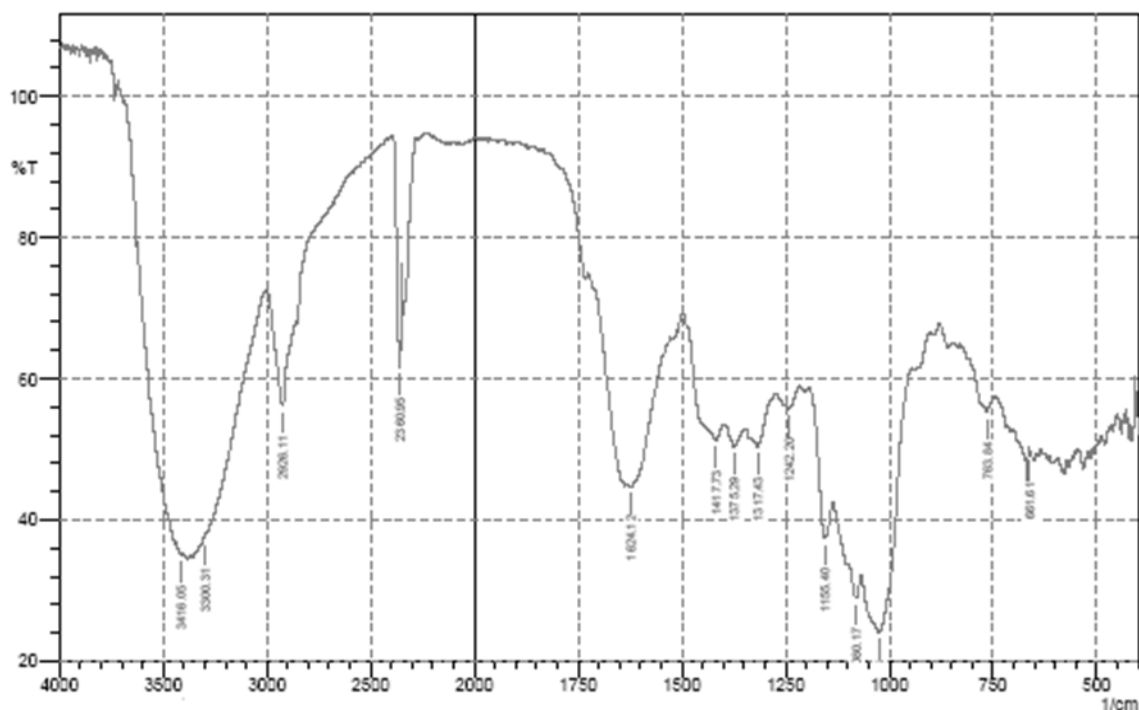


Fig. 8: Changes in nitrate concentration in the aqueous solution containing different concentrations of the treated raw plantain peel

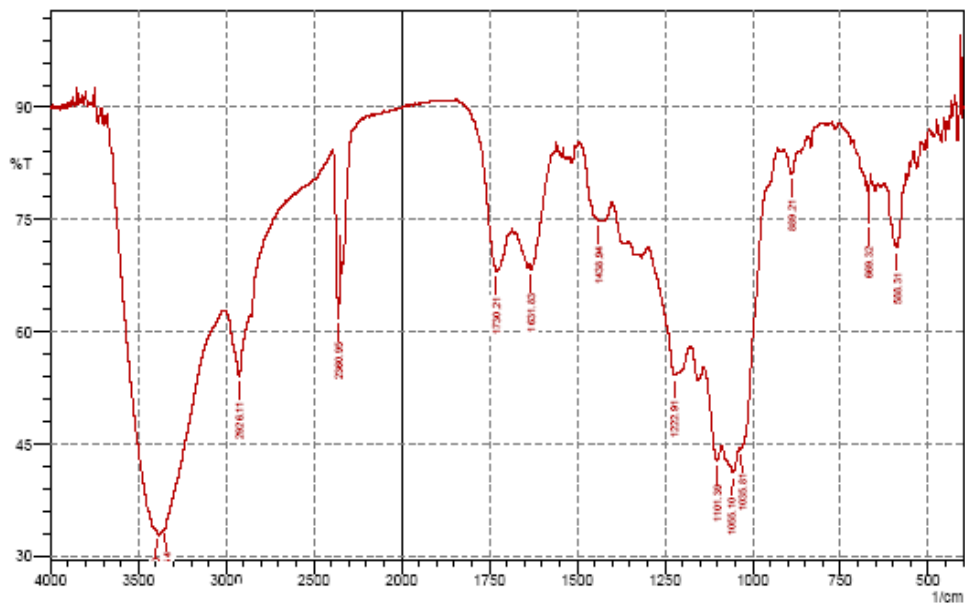
The presence of functional groups on the surfaces of the samples was determined using FTIR spectrophotometer and the spectra are shown in figures 9-12. A broad and intense absorption band was obtained at a range of 300 – 3416  $\text{cm}^{-1}$ , indicating the presence of intermolecularly and intramolecularly bound hydroxyl groups. Medium bands at 2926  $\text{cm}^{-1}$  and 1375  $\text{cm}^{-1}$  showed the presence of aliphatic C-H stretching and bending vibration, respectively. A strong absorption band at 1624  $\text{cm}^{-1}$  and a medium one of 1418  $\text{cm}^{-1}$  was indicative of an aromatic C=C stretching. A vinyl ether C-O stretching vibration was obtained at 1242  $\text{cm}^{-1}$  as a medium band while a strong absorption band of 1155  $\text{cm}^{-1}$  was an indication of the presence of C-O stretching vibrations of ether. A weak band of 1080  $\text{cm}^{-1}$  showed the presence of an alcoholic C-O stretching vibration

For the treated raw sample, additional absorption bands were obtained at 1101, 1222 and 1730  $\text{cm}^{-1}$ . These bands indicated the presence of C-O-C stretching vibration for a diaryl and a C=O stretching vibrations for a ketone or an  $\alpha$ ,  $\beta$ -unsaturated ester (Fig. 10).



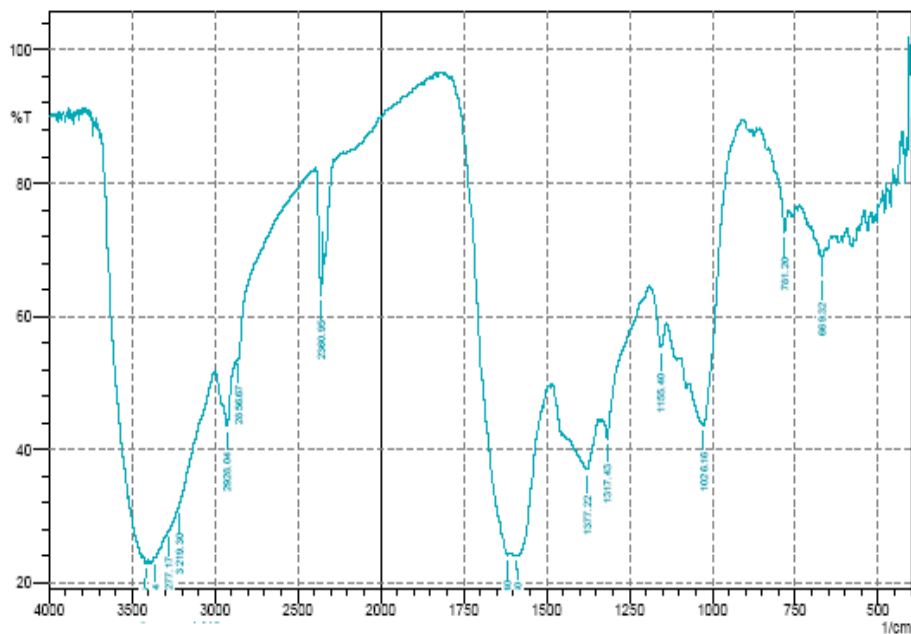
**Fig. 9: FTIR of the untreated raw peel**





**Fig. 10: FTIR of the treated raw peel**

For the carbonated untreated sample, a new band of medium absorption was obtained at  $2857\text{ cm}^{-1}$ , indicating the introduction of an alkyl group while the weak and medium absorption bands at  $1080\text{ cm}^{-1}$  and  $1242\text{ cm}^{-1}$ , respectively for vinyl ether were absent. For the carbonated treated sample, the C-O absorption bands for the vinyl ether and aromatic esters were absent while new bands were observed for C-H of the alkyl at  $2855\text{ cm}^{-1}$  and C=O stretching vibration at  $1699\text{ cm}^{-1}$ , which shows an oxidative reaction (Figs 11 and 12).



**Fig. 11: FTIR of the untreated carbonated peel**

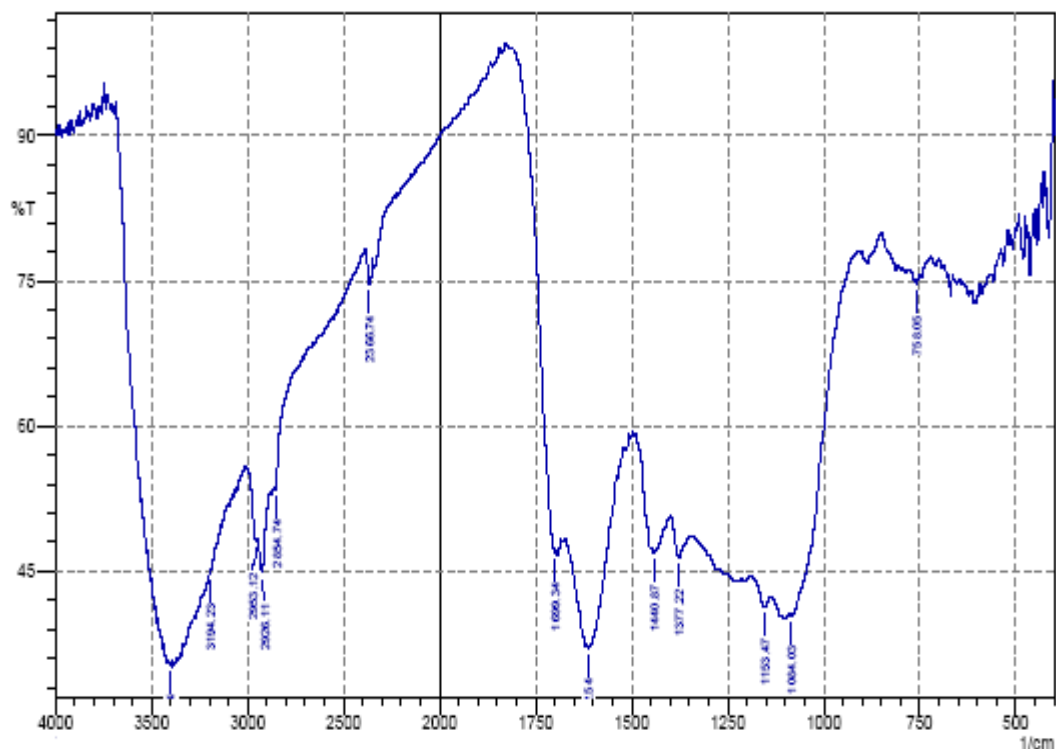


Fig. 12: FTIR of the treated carbonated peel

#### 4. Discussion

The present study revealed that the different modifications of the plantain peels used for this study have some measure of affinity for phosphate and nitrate ions in aqueous solution. The use of agrowaste thermally activated barks and stems of *Ficus religiosa*, *Cassia auriculata*, *Punicagranatum* and *Calotropis gigantean* have been reported to have remarkable affinity for phosphate ions (Jyothi *et al.*, 2012). Similarly, the use of ZnCl<sub>2</sub> activated coconut coir pith has been implicated for nitrate removal and recovery (Namasivayam and Sangeetha, 2005).

In this study, the form of treatment used for the raw and carbonated peels was activation with 20 % sulphuric acid. Acid modification of an agro waste absorbent has been reported by earlier workers (Ahmad *et al.*, 2009). According to Khan *et al.*, (2004), the activated carbon prepared by carbonization of rice husk with sulphuric acid followed by CO<sub>2</sub> activation gave a total chromium removal of 88 % and almost total removal of hexavalent chromium. Although the study did not compare different activation temperatures, it is reported that activation temperature, activation time and gasifying agents are determinants of the degree of development and widening of microporosity of an absorbent. It is argued that if activation conditions go beyond a certain level, it affects pore size of an absorbent. In such instances, the walls of the pores are reported to become so thin, hence collapsing and causing remarkable reductions in available surface areas (Huang *et al.*, 2008).

In a study by Chang *et al.*, (2000) on the effects of burn-off and activation temperature on preparation of activated carbon from corn cob agrowaste by CO<sub>2</sub> and steam, the comparison of all resulting activated carbons gave an indication that steam activation at 1173 K with low water flow rate can produce activated carbons while CO<sub>2</sub> activation at 1173 K was able to manufacture mesoporous activated carbons.

The present study revealed differing levels of nutrient removal among the different peel treatments. Also revealed in this study is higher nutrient removal at higher dosage levels of the peels. This trend was irrespective of the peels used. Earlier investigators have reported an increase in the biosorption percentage as dosage of biosorbent increases to certain level and then decreases. This was attributed to the availability of more binding sites in the surface of the biosorbent for complexation of ions in the solution (Muthusamy *et al.*, 2012). In a study by Muthusamy *et al.*, (2012), when maize cob was used for nickel removal from water, a 90 min contact

time was enough for saturation, after which there was a drastic decrease in absorption with further increase in contact time. The saturation time during this study was dependent on the type and dosage of peel used. It was also dependent on the nutrient being removed. In addition, the differing level of nutrient removal obtained with the different peel modifications may have been due to the differing levels of active pores found in the different modification. Ketcha and co-workers (2012) indicated in their work on activated carbons obtained from maize cobs by zinc chloride activation that the part of the cob used, the residence time, the quantity and state of the activating agent had effect on the extent of metal absorption.

## 5. Conclusion

This study, which was aimed at investigating the effectiveness of different modifications of plantain peel for the removal of phosphate and nitrate from aqueous solution, has revealed the following:

- Different modifications of the plantain peels used in the study has some measure of affinity for phosphate and nitrate removal
- The degree of removal of the nutrients is dependent on the modifications of the peels and the dosage of the peel

Although there is the need for further investigation to ascertain the best conditions for nutrient removal and the possibility for scale up studies, the present findings have revealed the potential of this agro-waste for use in the bioremediation of polluted wastewater effluents.

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