Numerically Optimized Effects of Contact Time Factor of Pulverized and Modified Bio-Adsorbents on Nitrogen Removal Rates in Industrial Wastewater

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ABSTRACT

This study investigated the effect of contact time of two agricultural wastes (cassava peels and ripe plantain peels) used as bio-adsorbents that were modified with base and acids to ascertain their ability to absorb nitrogenous compounds from hospital and abattoir wastewater. The absorbents were prepared using standard procedures into powdered forms and a portion was modified with acid and base respectively. Fourier Infrared spectroscopy was used on the prepared absorbents to determine the organic and functional groups present. Each modified bio-adsorbents was used to inoculate each of the 250 ml flasks containing the wastewater sample. Contact was allowed to be made for 14 hours and the nitrogen removal rate was measured and recorded. The Nitrogen concentration in the wastewater was determined using Ultra-violent spectroscopy. Response surface optimization was used to investigate the effect of contact time on the nitrogen removal rate. Models were generated to analyze the interactions between variables at optimum conditions. The results showed that the bio-adsorbents have the ability to remove nitrogen from wastewater. The nitrogen percentage removal recorded was 57%, 81%, and 77%, 55%, 91% ,and 78% respectively. The R^2 from ANOVA was seen to be 96.5%, 97.9%, 97.9%, 98.2%, and 99.7%, and 97.9% repectively. Experimental results were best fitted into linear and quadratic polynomial models. The optimum conditions having desirability of 0.964 showed that the time of 13.558 hrs. The values obtained are a good indicator that the bio adsorbents used in this should be considered by the chemical industries in the process of absorbent design and production.

INTRODUCTION

According to United Nations, one of the essential human rights is the availability of good drinking water [1]. Due to the conventional pollution of water sources, more than 800 million people lack access to good water [2]. Moreover, rapid growth in population and urbanization has brought about a high demand for potable and non-potable water. The growing trends of major industries in Nigeria channeling wastewater/effluents into the water bodies have raised a concern for the growing population in Nigeria.

The municipal wastewater comprises organisms (like pathogenic viruses and bacteria), wastewater/effluents discharged from hospitals and abattoirs, wastes from food and agriculture, decomposable organic materials, nutrients (such as ammonia, total phosphorus, and nitrogen) other organic substances (like fat, pesticides, detergents, etc.), inorganic materials, metals (iron, lead, mercury). These causes harm not just to humans and the environment but also the ecosystem [3].

Although nitrate is an essential plant nutrient, in excess can cause significant water quality problems. Some of these problems are eutrophication, which can stimulate the growth of algae [4]. Increased water purification cost, interference with the recreational value of water, and health risks to humans and livestock [5]. Nitrogenous chemicals which are oxidized from excess nitrogen present in wastewater from industries are responsible for cancer and blue baby syndrome [6].

Studies have also found that exposure to high concentrations of nitrates can result in serious illness and death of infants and pregnant women, increased risk of neural tube defects, premature birth, intrauterine growth restrictions, and congenital malformations [7].

Additional known or suspected health effects on children and adults include respiratory tract infections in children, thyroid disruption, pancreatitis, sudden infant death syndrome [8], and cancers of the digestive system, bladder, and thyroid [7, 9-13]

The importance of removing nitrogen and phosphorous from industries and municipal wastewater has increased significantly over the past decade to minimize water pollution and avoid the eutrophication of water bodies [14]. Nitrogenous compounds present in wastewater/effluents are mostly organic nitrogen, ammonium/ammonia, and nitrate. It must be treated to meet stringent effluent requirements imposed by legislation [15].

This study was therefore aimed at investigating the optimized effects of contact time of modified bio-absorbent peels of cassava (*Manihot esculenta)* and ripe plantain peels (*Musa paradisiaca*) in the removal of nitrate or reducing its concentration from wastewater channeled in water bodies by industries.

LITERATURE REVIEW

Industrially, Nitrogen-containing substances are removed by silica gel through physisorption [16]. The attraction between the adsorbent and polar nitrogen molecules in silica gel is mediated by hydrogen bonding [17], which promotes silica regeneration because silica gel lacks strong adsorptive sites, the adsorbed nitrogen compounds were then subjected to gas chromatography-mass spectrometry (GC-MS) analysis.

The adsorbent, a solid substance, is used in adsorption operations to remove nitrogen-containing compounds from wastewater by holding on to the nitrate when the adsorbent passes over it [18]. The material for the adsorbent is chosen so that interactions with its surface would draw and hold nitrogen-containing molecules.

Chemical or physical interactions with a substance can cause it to absorb the nitrogen compounds on the surface. A chemical connection is created between the adsorbent and the substance through a chemical interaction that also alters the compound's electronic structure [19]. The compound keeps its identity and no new bonds are created when it is maintained on the surface by a physical interaction such as van der Waals or electrostatic forces. The strength of retention and selectivity is influenced by the type of contact period and other necessary parameters that this study tends to explore. Because it uses the chemical identity of the nitrogen-containing chemicals and retains the compounds more effectively [20], chemisorption is typically more selective. Even though silica gel is exclusively physisorbed nitrogen-containing chemicals, it seemed to be extremely selective for these substances [21]. Before hydrotreating, silica gel pretreatment of light cycle oil (LCO) allowed for a reduction in nitrogen level from 635 to 16 ppm while leaving the sulfur and aromatic contents unaltered [22]. This is helpful during adsorption, but it also makes it more challenging to remove the adsorbed molecules when the adsorbent is regenerated for reuse, hence the need to look beyond the conventional chemicals into naturally occurring bio-substances that are cheap and readily available [23].

MATERIALS AND METHODS
Sourcing of Materials

Wastewater mixture discharge from Central hospital and Abbatoirs both in Agbor was collected in a clean plastic container from Orogodo River in Agbor, Delta State. The collected samples were transported in an ice chest to the University of Benin Laboratory and preserved in the refrigerator until used.

The fresh peels from *Manihot esculenta* and ripe *Musa paradisiaca (cassava and ripe plaintain)* used as adsorbents were collected from a farm produce market in Abavo, Delta State, and were separately packed in perforated sack bags.

Methodology
Adsorbents Preparation

In this study, cassava peels and ripe plantain peels were used as adsorbents. The peels were rinsed thoroughly with clean water to remove debris and other impurities. Peels were sun-dried to a constant weight for 5 days. After which the clean peels were pulverized into a fine powder using a sterilized food mill. The

powdered peels were sieved using a sieve of 500 microns pore size. The pulverized powders were stored respectively in their various air-tight plastic containers at room temperature until use or further treatment.

Three different forms of pulverized cassava peels were used. They are the raw pulverized cassava peel without any form of modification (labeled as CU), pulverized peels with acidic modification (labeled as CA), and pulverized peels with base modification (labeled as CB). CA was prepared by soaking the pulverized cassava powder with 50% activated concentrated sulphuric acid for 2 hours. This is then followed by washing with distilled water until all traces of the acid is removed. This was confirmed by the litmus paper test. The activated cassava peels were recovered by using Whatman No.1 filter paper. The filtrate was then oven-dried at 120°C for 5 hours to remove all traces of water. The dried activated cassava peels were then stored in a dried plastic container at room temperature.

The third form of the pulverized cassava powder (labeled as CB) was prepared by also soaking with 50% activated Sodium hydroxide and the same procedures as above were carefully repeated.

The ripe plantain peels were cut into pieces and rinsed thoroughly with clean water to remove debris and other impurities. The plantain peels were dried in an oven to a constant weight at a temperature of 60°C for 7 days. After which they were pulverized into a 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.

The pulverized plantain powder used for this study was also of three forms. The same procedures were carefully repeated to obtain pulverized plantain powder without modification labeled as PU, PA was labeled on the container with pulverized plantain powder with sulphuric acid modifications and lastly labeled airtight container PB with pulverized powder with Sodium hydroxide modifications. The same laboratory procedures were strictly followed as earlier discussed for the ripe plantain powder modifications.

Determination of Functional Group

Fourier Transform Infra-Red (FTIR) spectroscopy was carried out to analyze the functional groups and the changes that have taken place in the structure of cassava and plantain peels as a result of modification by acid and base activations.

The chemical structure of the adsorbent is vital to the understanding of the adsorption process. The FTIR of cassava and plantain peel unmodified and modified with acid and base were carried out as a qualitative analysis to gain better insight into the functional groups available on the surface of the investigated adsorbent. The FTIR spectra measured within the range of 4000 cm^{-1} – 500 cm^{-1}.

Experimental Determination of Nitrogen from Wastewater Sample

A nitrogenous compound present in wastewater in this study was determined using a UV spectrophotometer. A standard solution of nitrate was made by dissolving 1g of potassium nitrate (KNO_3) in 1 L of distilled water to give a 1000mg/L stock solution of KNO_3. Serial dilutions from stock solution were done for the preparation of calibration standards for nitrate in the range of 0.1–1.0 mg/L. A test tube stands with several reaction tubes set up inside was placed in a cold water bath. The wastewater sample was measured and poured into the tubes with KCl solution and sulphuric acid added respectively. The mixture was heated for a few minutes in a boiling water bath after adding brucine-sulphanilic acid reagent. It was allowed to cool for absorbance measurement from the calibration curve.

Determination of Contact Time

2 g each of the prepared adsorbent (CU, CA, CB, PU, PA, and PB) was weighed into six different 250ml capacity flasks containing 50ml of the wastewater sample each, and mixing was done utilizing a mechanical stirrer. Another flask containing 50ml of only wastewater was also set up to act as the control. For every 2 hours, the mixtures in each flask including the control were withdrawn and contents are made to pass through Whatman No 1 filtered paper. The filtrates were then analyzed for nitrate concentration using standard procedures.
Equation (1) was used in the determination of the percentage removal of the nitrate present as a result of the interaction of the adsorbents and the wastewater

$$\%R = \frac{c_{i} - c_{a}}{ci} \times 100 \qquad (1)$$

Where Ci and C_a are the initial nitrogen concentration in wastewater and the absorbed concentration of nitrogen after interaction with wastewater [24]

Experimental Design

Response surface methodology was used to investigate the effect of the independent variable; contact time (X1) on response variables such as removal rate using Cu (Y1), CA (Y2), CB (Y3), PU (Y4), PA(Y5) and PB(Y6). Estimating coefficients, predicting responses, and determining whether the resulting model is acceptable are all steps in system optimization.

$$Y = f(X_1 \ldots X_n \pm \varepsilon) \qquad (2)$$

Where Y is the response, f is the response function, $X_1 \ldots X_n$ is the independent variables, and ε is the experimental error.
One factor Design Matrix was used and response values of percentage removal were obtained experimentally using the bio-adsorbents. The predicted responses (Y_1, $Y_2 \ldots Y_6$) as a function of an independent variable depend largely on the interaction between the independent variable and the response variable using a second-order polynomial equation. [25]

$$Y = b_o + \sum b_i x_i + \sum b_{ii} x_{ii}^2 + \sum b_{ij} x_i x_j + \varepsilon \qquad (3)$$

Where Y is the predicted response, b_0 is the intercept, and b_i, b_{ii}, b_{ij} represents the linear, quadratic, and interaction coefficients. X_i and X_j are coded values of the process variables and experimented error denoted as ε.

Using Design Expert Software Stat-Ease (version 13.0.11), experimental data were statistically analyzed. To choose the most appropriate polynomial model, statistical measures including lack-of-fit, predicted, and adjusted multiple correlation coefficients of various polynomial models were examined. Through analysis of variance, a significant difference was identified by determining the F-value at the probability function. Response plots were equally generated using Design Expert to examine the impact of contact time on the response variables.

RESULTS AND DISCUSSION
FTIR Analysis

Cassava Peels

Fig. 1-3 showed the FTIR results of the various categories of cassava peels used in this study. Transmittance was plotted against wave number. The FTIR study for the unmodified cassava peels is presented in Fig. 1, the band in the region of 3277.54cm^{-1} were assigned to O-H stretch (alcohol and phenols), the sharp band at 2918.69cm^{-1} indicates a C-H stretch (acids, carboxylic) while those at 1629.49cm^{-1} signifies the presence of C=C stretch indicating the alkenes compounds
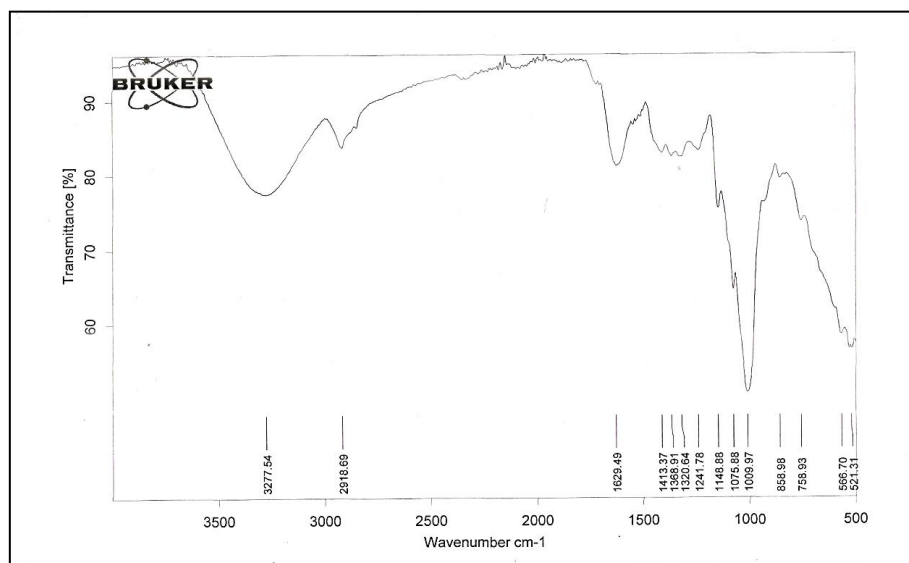

***Figure 1:** FTIR spectrum for unmodified cassava peels.*

For the FTIR of the acid-modified cassava peels in Fig. 2, adsorption peaks at the bands 3325.35 cm^{-1} and 3276.66 cm^{-1} were attributed to O-H stretch which indicates alcohols and phenols compounds. The band at 1724.64cm^{-1} region shows C=O stretch (aldehydes) at 1631.66cm^{-1} signifies the alkenes groups.
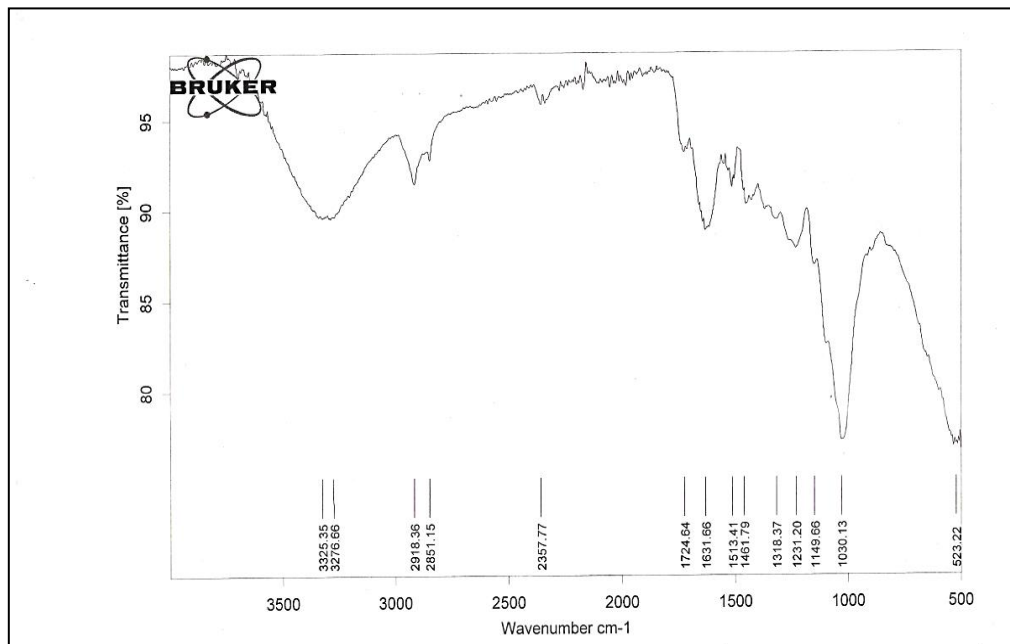

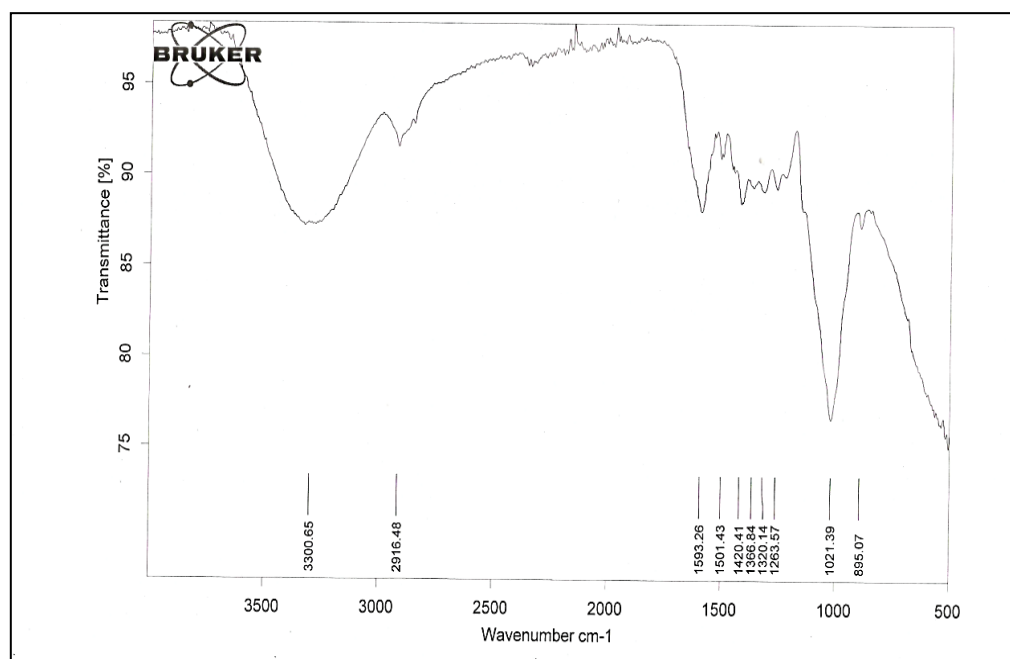*Figure 2: FTIR spectrum for acid-modified cassava peels.*

Figure 3: FTIR spectrum for base-modified cassava peels.

For the base-modified cassava peels Fig. 3, the adsorption peak at 3300.65 cm^{-1} is an O-H stretch (alcohols and phenols) and the peak at region 2916.48cm^{-1} were attributed to O-H stretch (acids, carboxylic compounds) and 1593.26cm^{-1} confirms the C=C stretch of the alkenes functional group.

However, comparing Fig. 1, 2, and 3, we could see that most bands' positions did not change following modification; this suggests that the cassava peels structure did not collapse upon modification.
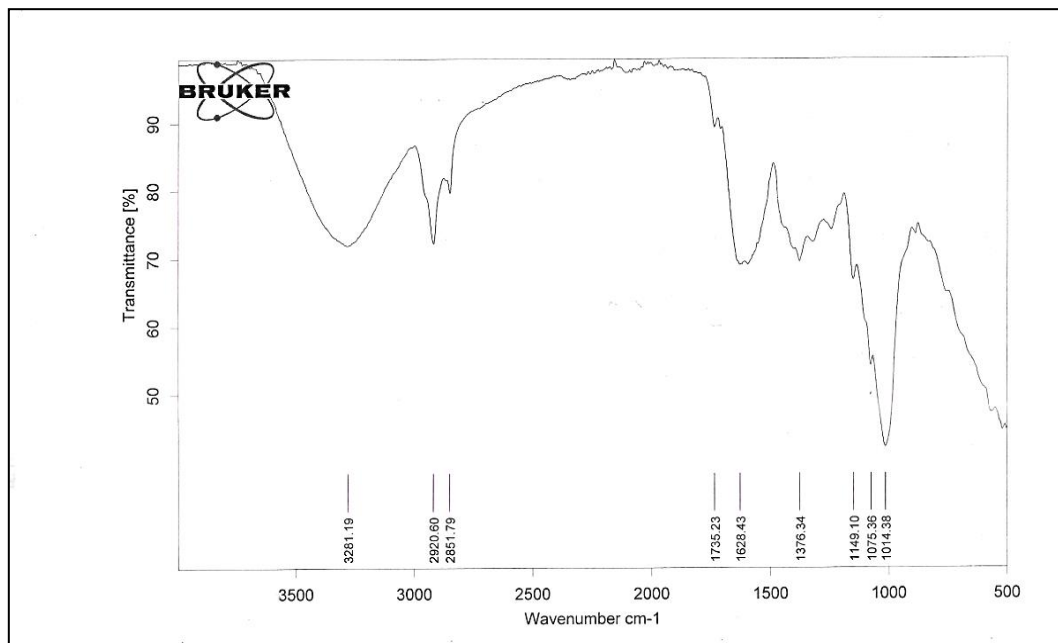
Plantain Peels

Figure 4: *FTIR spectrum for unmodified plantain peels.*

From Fig. 4, it was observed that the FTIR spectra of unmodified plantain peels showed the band at $3281.19 cm^{-1}$ which was due to O-H stretch while the bands at $2920.60 cm^{-1}$, $2851.79 cm^{-1}$ $1735.23 cm^{-1}$ $1628.43 cm^{-1}$ and $1376.34 cm^{-1}$ were assigned to O-H stretch (acids, carboxylic), C-H stretch (alkyl groups), C=O stretch (esters), N-H bend (amines) and C-H bend (methyl) respectively.

In Fig. 5, the FTIR spectra of acid-modified plantain peels band at $3289.39 cm^{-1}$ is due to O-H stretch (alcohol, phenol), the sharp peak at $2920.44 cm^{-1}$ indicates an O-H stretch also but of acid, carboxylic functional group. At $2852.29 cm^{-1}$ there is another sharp peak indicating C-H stretch (alkyl group) while at regions $1630.40 cm^{-1}$ and $1441.81 cm^{-1}$ we have N-H bend (amines) and C-H bend (alkyl groups) respectively.
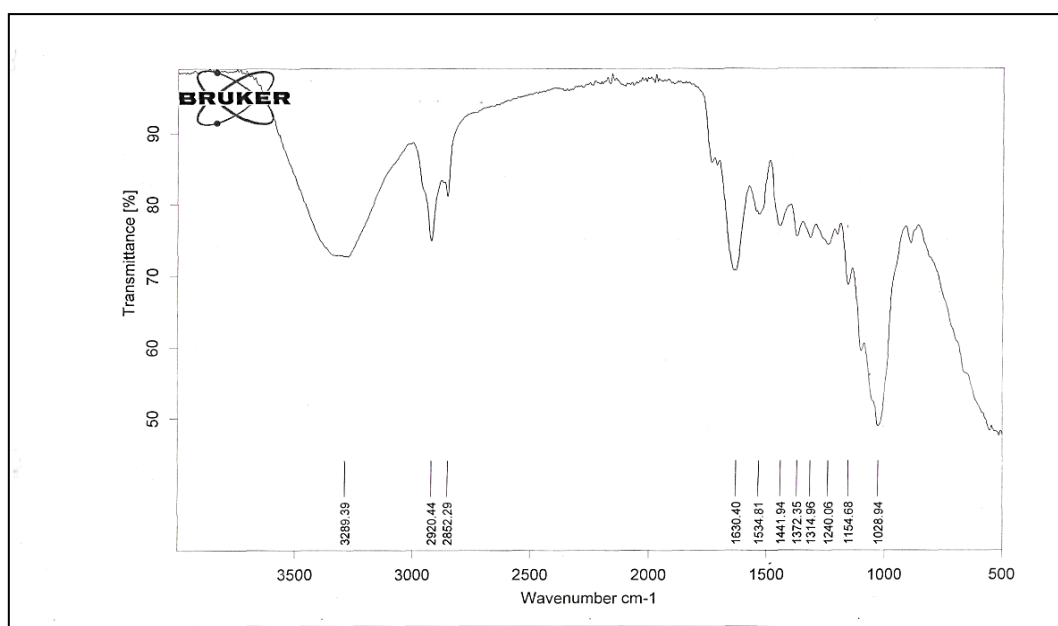

Figure 5: *FTIR spectrum for acid-modified plantain peels.*

The presence of O-H stretch (alcohols, phenols) was observed in Fig. 6, at region 3325.66cm^{-1} while another O-H stretch (due to acids carboxylic groups) was observed at 2917.50cm region and 1630.57cm^{-1} bands, N-H bend (amine) was observed.
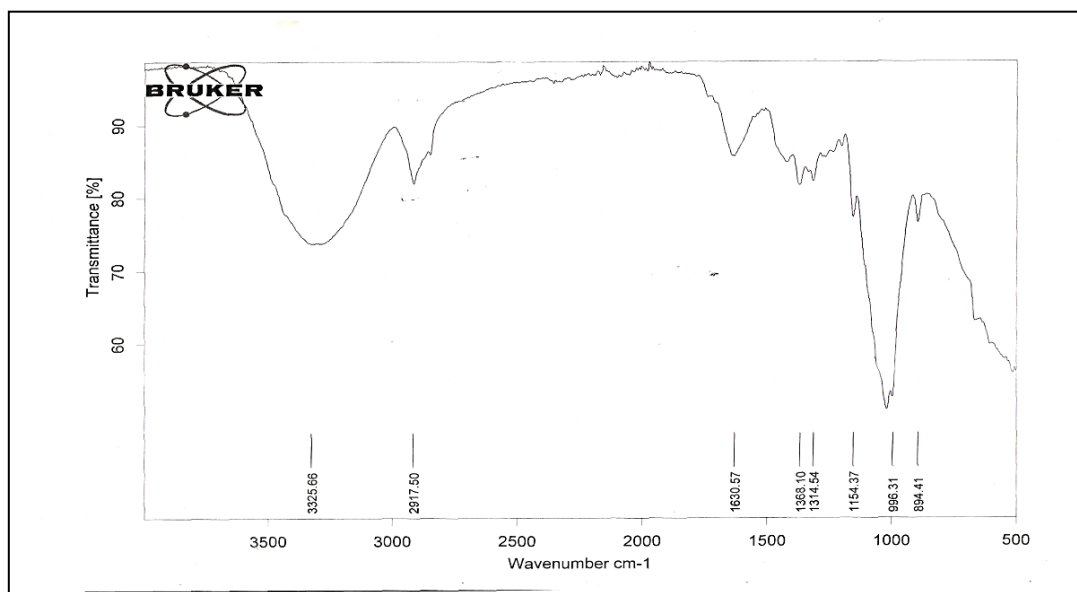

Figure 6: FTIR spectrum for base-modified plantain peels.

Comparing (Fig. 4, 5, and 6), we could see that there were changes due to the modifications but the modifications did not destroy the entire structures.

Effect of Contact Time

Table 1: Concentrations and percentage removal of nitrates for the effect of contact time.

Time (hrs)	Control	CU		CA		CB		PU		PA		PB	
		mg/l	%R	mg/l	%R	mg/l	%R	mg/l	%R	mg/l	%R	mg/l	%R
1	273.12	271.1	1	230.02	15	232.53	15	241.81	11	184.39	32	187.54	31
2	273.12	269.80	1	218.05	20	219.34	20	230.19	16	152.02	44	160.38	41
3	273.12	267.92	2	203.58	25	190.45	30	216.56	21	122.11	55	134.26	51
4	273.12	252.46	8	143.01	48	141.46	48	185.86	32	108.96	60	110.38	60
6	273.12	205.20	25	113.44	58	113.7	58	145.51	47	72.54	73	102.9	62
8	273.12	196.82	28	86.01	69	81.12	70	132.28	52	43.91	84	71.47	74
10	273.12	180.49	34	67.94	75	67.94	69	127.4	53	24.69	91	58.9	78
12	273.12	118.06	57	51.65	81	51.65	77	122.66	55	24.69	91	58.9	78
14	273.12	118.06	57	51.65	81	51.65	77	122.66	55	24.69	91	58.9	78

The experimental result on the effect of contact time on nitrogen absorbance measurement and percentage removal rate is as shown in Table 1; it took 14 hours for equilibrium to be reached by the cassava peels irrespective of the kind of modifications. Equilibrium is attained when the absorbent pores and surface area are unable to absorb any further concentration of the nitrates [25]. It can be observed from Table 1, that the progressive increase in contact time did not show a notable change in equilibrium concentration and percentage removal of the nitrogen. This is in line with the study of [26] which reported that the adsorption process will be constant after the surface of the active adsorbent approaches saturation.

A nitrogen removal rate of 1% to 57% was calculated for unmodified cassava peel within the period for which equilibrium was attained. 15% to 81% of nitrogen concentration was removed when cassava peel modified with acid was used. The base-modified nitrogen removal rate was calculated to be from 15% to 77%.

For the modified plantain peels, the adsorption rate tends to be faster in the early hours, especially for the modified plantain peels. The unmodified plantain peel was calculated to have a removal rate of 11% to 55%, the acid-modified from 32 % to 91%, and the base modified from 31% to 78%. The result showed that the acid-modified plantain peel is a better adsorbent for nitrate since it was able to remove 91% of the nitrate from the wastewater sample.

Comparatively, the unmodified cassava can absorb more of the nitrate (57%) than the unmodified plantain having a removal rate of 55%. The acid-modified cassava was able to absorb 81% of nitrate concentration from the sample while the acid-modified plantain peel adsorbed 91% of the nitrate making it a better adsorbent likewise the base-modified plantain peel adsorbed more of the nitrate (78.%) than the base modified cassava that adsorbed 77 % of nitrate at equilibrium time.

Effect of Contact Time on Percentage Removal of Nitrates from Wastewater Using Response Surface Methodology
Statistical Analysis

Statistical information for the ANOVA summary table for all the responses shows that the models describing CU, CA, CB, PU, PA, and PB had a high coefficient of determination (R^2) as shown in Table 2. This shows that the models were able to adequately represent the relationship between the independent variable (contact time) and responses (CU, CA, CB, PU, PA, and PB). R^2 values of 0.965,0.979,0.979,0.982,0.997, and 0.979 means that the models were able to explain 96.5%, 97.9%, 97.9%, 98.2%, 99.7% and 97.9% of the variability observed in the values of CU, CA, CB, PU, PA, and PB respectively. The standard deviations were observed to be relatively small compared to the mean. The coefficient of variation was obtained for the six models as 18.39, 8.50, 7.88, 7.42, 2.12, and 4.73 respectively. Also from Table 2, there is reasonable agreement between the predicted R square value and the adjusted R squared value since their differences are less than 0.2. Hence the model can be used to navigate the design space.

Table 2: Statistical information for ANOVA.

Parameter	Responses					
	CU	**CA**	**CB**	**PU**	**PA**	**PB**
R-Squared	0.9651	0.9790	0.9793	0.9818	0.9968	0.9792
Mean	21.78	52.44	51.56	38.00	69.00	61.44
Standard Deviation	4.00	4.46	4.06	2.82	1.46	2.91
C.V%	18.39	8.50	7.88	7.42	2.12	4.73
Adeq. Precision	29.422	26.980	27.247	29.235	69.500	27.294
Adjusted R-Square	0.9601	0.9720	0.9724	0.9757	0.9957	0.9723
Pred R-Squared	0.9383	0.9615	0.9577	0.9572	0.9927	0.9546

Equations (4-9) were obtained after applying multiple regression analysis to the experimental data. Linear and quadratic equations were used for the evaluation of the responses, for CU first-degree polynomial while CA, CB, PU, PA, and PB second-degree

polynomial respectively.

$$Y_1 = +25.34 + 27.77\ X_1 \qquad (4)$$
$$Y_2 = +66.12 + 34.71\ X_1 - 19.89\ X_1^2 \qquad (5)$$
$$Y_3 = +65.32 + 31.31\ X_1 - 21.04\ X_1^2 \qquad (6)$$
$$Y_4 = +49.22 + 22.59\ X_1 - 17.95\ X_1^2 \qquad (7)$$
$$Y_5 = +81.92 + 28.58\ X_1 - 19.97 X_1^2 \qquad (8)$$
$$Y_6 = +72.12 + 21.84\ X_1 - 16.99 X_1^2 \qquad (9)$$

Where, Y_1, Y_2, Y_3, Y_4, Y_5 and Y_6 = predicted responses for CU, CA, CB, PU, PA, and PB respectively, X_1= A coded levels of contact time. The values of Y_1, Y_2, Y_3, Y_4, Y_5, and Y_6

predicted by Equations (4-9) are given in Tables 3 and 4 along with their respective experimental data. The significance of the fit of the equations representing CU, CA, CB, PU, PA, and PB was evaluated by carrying out an analysis of variance. ANOVA results show that the models for CU, CA, CB, PU, PA, and PB were statistically significant with p values of <0.0001, <0.0001, <0.0001, <0.0001, <0.0001 and <0.0001 respectively. Since p values of ("Prob> F"), less than 0.0500 indicate model terms are significant for the six models.

Table 3: Model validation table for cassava peels.

Run No	Variable (Time) (hrs)		Responses					
	Coded level	Actual Value	CU (%R)		CA(%R)		CB(%R)	
	X1	X1	Actual	Predicted(Y_1)	Actual	Predicted(Y_2)	Actual	Predicted(Y_3)
1	-0.231	6	25	19	58	57	58	57
2	-0.846	2	1	2	20	23	20	24
3	-1.000	1	1	-2	15	12	15	13
4	-0.692	3	2	3	25	33	30	34
5	0.385	10	34	36	75	77	69	74
6	0.077	8	28	27	69	69	70	68
7	0.692	12	40	44	81	81	77	77
8	-0.538	4	8	10	48	42	48	42
9	1.000	14	57	53	81	81	77	76

Table 4: Model validation table for plantain peels.

Run No	Variable (Time) (hrs)		Responses					
	Coded level	Actual Value	PU (%R)		PA (%R)		PB (%R)	
	X1	X1	Actual	Predicted(Y_4)	Actual	Predicted(Y_5)	Actual	Predicted(Y_6)
1	-0.231	6	47	43	73	74	62	66
2	-0.846	2	16	17	44	43	41	42
3	-1.000	1	11	9	32	33	31	33
4	-0.692	3	21	25	55	53	51	49
5	0.385	10	53	55	91	90	78	78
6	0.077	8	52	51	84	84.	74	74
7	0.692	12	55	56	91	92	78	79
8	-0.538	4	32	32	60	61	60	55
9	1.000	14	55	54	91	91	78	77

Optimization of the Effect of Contact Time on Percentage Removal of Nitrates from Wastewater

Response surface methodology was used to optimize the experimental variable. This was achieved by designing response surface plots showing the effect of contact time on the percentage removal of nitrate using the bio-adsorbents from wastewater. Fig. 7-12 shows the effect of contact time on CU, CA, CB, PU, PA, and PB. The trend observed shows that the CU has a linear increase with an increase in the contact time while CA, CB, PU, PA, and PB have a second-degree polynomial increase concerning contact time.
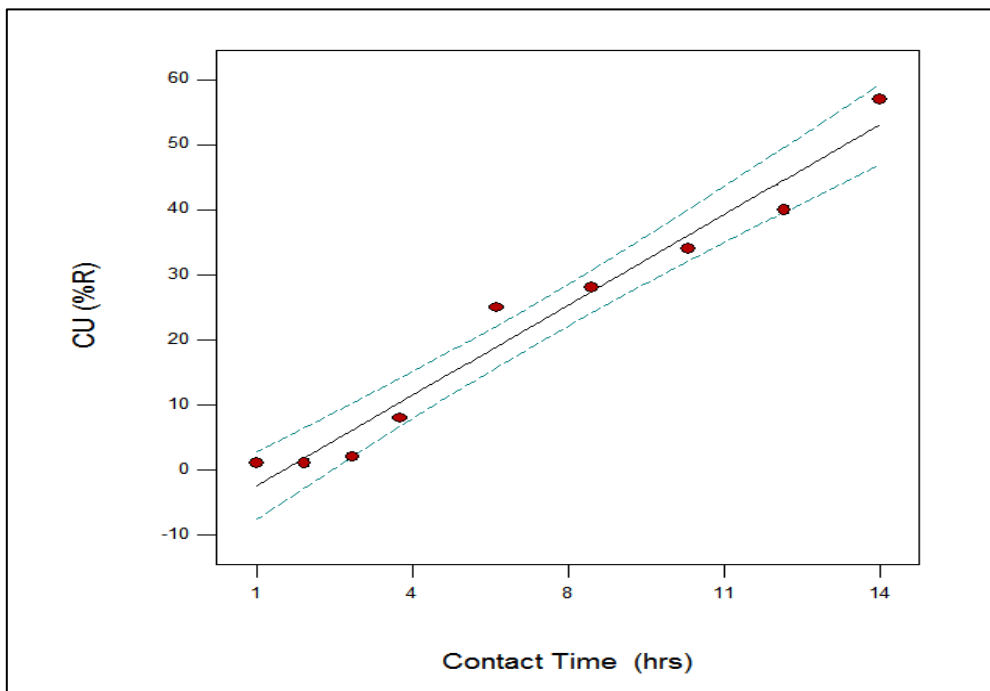
Figure 7: Effect of contact time on CU.
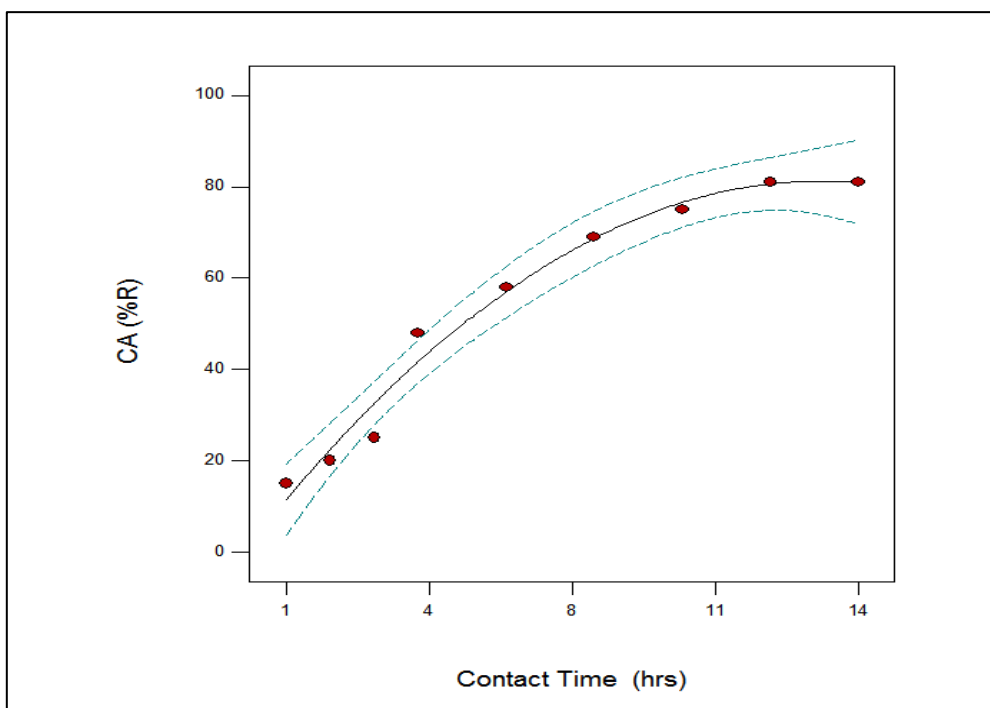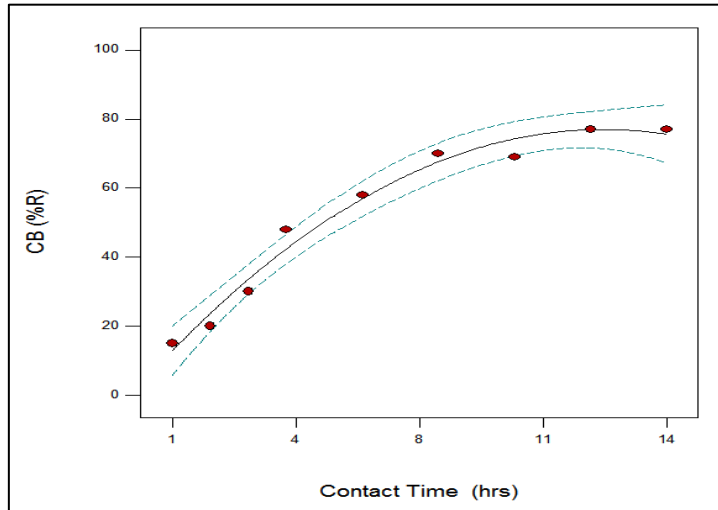

Figure 8: Effect of contact time on CA

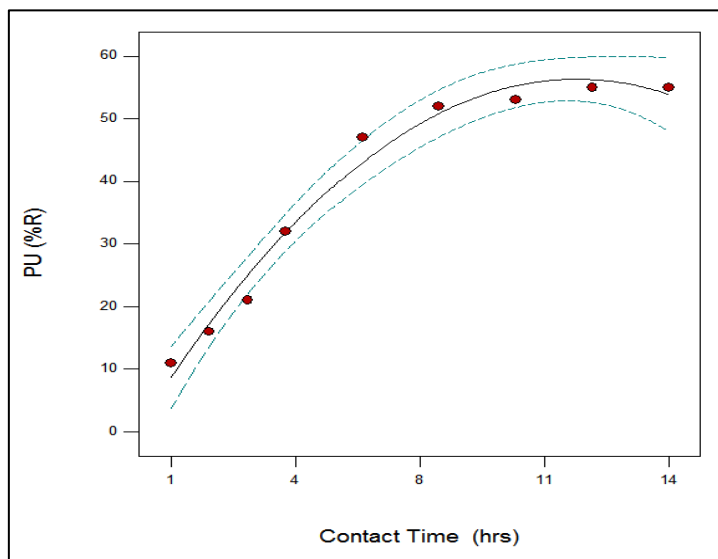*Figure 9: Effect of contact time on CB.*

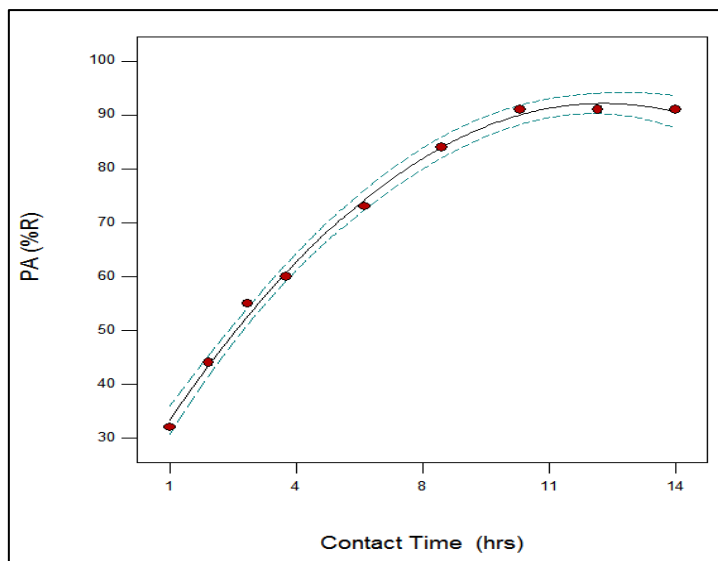

Figure 10: Effect of contact time on PU.
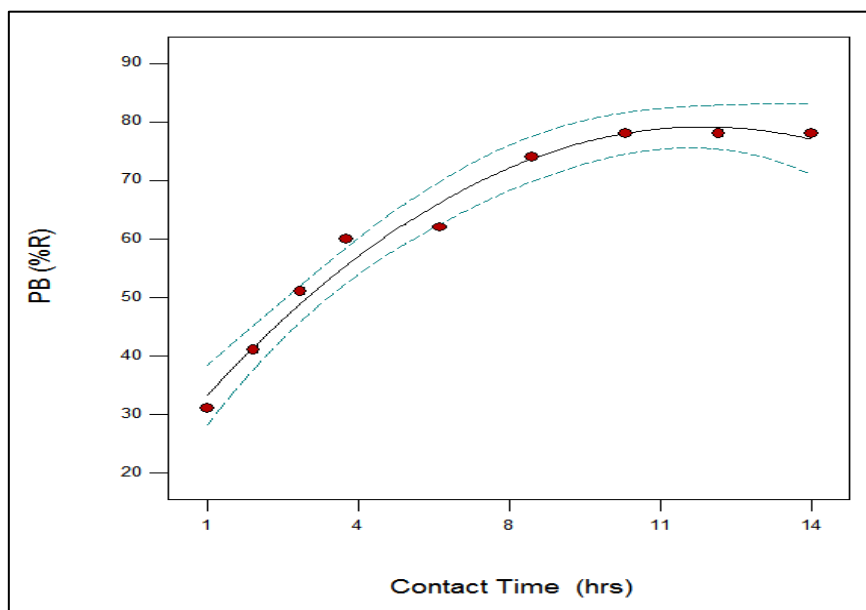

Figure 11: Effect of contact time on PA.

Figure 12: *Effect of contact time on PB.*

The optimum conditions of the independent variable (contact time) and the responses (percentage removal of CU, CA, CB, PU, PA, and PB) were determined from numerical optimization of the statistical models and the top three results are shown in Table 5. The results show that the maximum CU, CA, CB, PU, PA, and PB was obtained at a contact time of 13.558hrs as can be seen from table 4. The values of the percentage removal of CU, CA, CB, PU, PA, and PB obtain at most optimized conditions were 51.223%R,

81.184%R, 76.222%R, 54.674%R, 91.204%R, and 77.719%R respectively.

The number of active centers in a certain adsorbent can be further activated and modified after impregnation to improve the pore size and pore volume [27]. From Table 5, the bio-adsorbent materials' increase in pore size and volume, caused by acid and base activation, contributed to the increase in the value of the percentage removal of CA, CB, PA, and PB, thereby improving their adsorption capacity.

Table 5: *Solutions for optimum conditions.*

Solution Number	Contact time	CU(%R)	CA(%R)	CB(%R)	PU(%R)	PA(%R)	PB(%R)	Desirability
1	13.558	51.223	81.184	76.222	54.674	91.204	77.719	0.964
2	13.607	51.430	81.165	76.162	54.592	91.138	77.645	0.964
3	13.512	51.024	81.200	76.278	54.751	91.265	77.789	0.964

CONCLUSION

This study revealed that the six samples of the adsorbents (CU, CA, CB, PU, PA, and PB) which to a great extent is an agricultural waste can be of great importance and a cheap substitute for the ever-expensive chemical absorbent. Industries and hospitals can now comfortably treat their wastewater before discharging it into water bodies without much cost burden on them.

These absorbents have all shown different measures of affinity in the removal of nitrate ions from industrial effluents. The extent of removal of the nitrate is dependent on the modifications of the peels and the contact time. A nitrogen removal rate of 57% (from 271.12mg/l to 118.06mg/l) was calculated for unmodified cassava peel within the period for which equilibrium was attained as the .81% of nitrogen concentration was removed when cassava peel modified with acid was used. The

base-modified nitrogen removal rate was calculated to be 77%.

For the modified plantain peels, the adsorption rate was faster at the beginning of the experiment, especially for the modified plantain peels. The unmodified plantain peel was calculated to have a removal rate of 11% to 55%, the acid-modified from 32 % to 91%, and the base modified from 31% to 78%.

R^2 values of 96.5%, 97.9%, 97.9%, 98.2%, 99.7%, and 97.9% obtained from the ANOVA analysis were all close to 1 which signifies that the model equations generated for the response of CU, CA, CB, PU, PA, and PB respectively will successfully be used to navigate the design space. The optimum condition was obtained through numerical optimization using the desirability function. The solutions for optimum conditions having desirability of 0.964 showed that the time of 13.558hrs could yield nitrogen removal rates of 51.223%, 81.184%, 76.222%, 54.674%, 91.204%, and 77.719% respectively.

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