Removal of COD and Ammoniacal-Nitrogen from Industrial Wastewater using Adsorption with Plantain Husk Adsorbent

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ABSTRACT

The rate of depletion of ground/surface water has increased due to the weakness in the existing laws, contamination of the ground water and excess usage of water that produce increased quantity of wastewater. In this study, wastewater from Dangote Fertilizer Limited (DFL) was treated using adsorption method of treatment with consideration of the factors (pH, temperature and contact time) that impedes the efficiency of the method. Plantain husk, which is an agricultural waste, was used as adsorbent in the adsorption process. Response Surface Methodology (RSM) was used to determine the experimental number of runs after which it gives the optimum conditions of those parameters considered. The plantain husk was characterized using Gas chromatograph with Flame Ionization detector (GC-FID). The results obtained in the study revealed that utilization of the plantain husk as adsorbent in adsorption process for the removal of COD and Ammoniacal nitrogen from industrial wastewater will yield a high percentage removal (values). Ammoniacal nitrogen removal with plantain husk adsorbent was about 93% maximum and as pH increased to 7.5 (alkaline), a slight decrease in the Ammoniacal nitrogen removal percentage to about 92% could be attained. Furthermore, percentage removal of COD from the wastewater of about 83% maximum could be obtained. Effect of temperature on COD removal is a direct correlation as increase in temperature could lead to the decrease in COD removal. It can be concluded that the interaction between contact time and pH as compared to other interactions has an overall positive effect in the adsorption process of Ammoniacal nitrogen removal from wastewater. Being an agricultural waste and environmentally friendly materials, adsorbent from plantain husk should be considered for treatment of industrial waste water for removal of COD and ammoniacal nitrogen.

Keywords-- Ammoniacal Nitrogen, Chemical Oxygen Demand (COD), Adsorption, Plantain Husk

I. INTRODUCTION

Water is used extensively in the petroleum and petrochemical industries worldwide for various industrial operations, which include employing it as a reactant, solvent, cleaning/stripping agent, steam production, cooling, and boiler water. The aforementioned needs are satisfied utilizing the few freshwater resources, including surface water, groundwater, ocean, and recycled water, resulting in wastewater that, if not treated, can be hazardous to the environment. The large amount of water used in these industries results in industrial wastewater, which is then released into the environment, raising serious concerns and posing a number of environmental hazards because it contains several pollutants, including the biggest polluters of water sources in the environment: ammonia, hydrogen sulfide, mercury, arsenic, etc. Therefore, reducing water use and treating wastewater to make it reusable and less hazardous is very vital (Breida et al., 2019).

Wastewater released from those petrochemical and petroleum sectors comprises a small number of pollutants that are classified as nutrients, refractory organics, volatile organic compounds (VOCs), heavy metals, and physical and chemical contaminants (Ref Reqd). Characteristics of wastewater are frequently defined in terms of Chemical Oxygen Demand (COD), Biochemical Oxygen Demand (BOD) and BOD5, Total Organic Carbon (TOC), and Total Suspended Solids (TSS) (**Ref. reqd**).

The quantity of oxygen needed to oxidize both organic and inorganic molecules in water is known as the chemical oxygen demand. This COD test measures the amount of dissolved oxygen that the contaminants must consume, and its result is directly inversely related to the number of pollutants present in the sample. Chemical Oxygen Demand (COD) levels in wastewater discharged from fertilizer factories typically range from 111.36 to 293.12 mg/l, making it harmful to the environment and necessitating treatment (**ref reqd**).

Nutrients like phosphorus and nitrogen, as well as their compounds, in particular waste water from nitrogenous fertilizer industries, which contains ammoniacal nitrogen in extremely high concentrations and can cause serious issues like eutrophication, the loss of dissolved oxygen, and toxicity in aquatic life in lakes, rivers, and other bodies of water (Jellali et al., 2011). The highly poisonous ammonia (NH_3) molecules that make up the nitrogen component of refinery wastewater pollution are a concern to both aquatic life and human health. Untreated wastewater from fertilizer factories also contains phosphate (PO_4^{3-}) from 5 to 64 mg/l, ammoniacal nitrogen (NH_3-N) from 56 to 652, and nitrate-nitrogen (NO_3-N) from 100 to 400 mg/l (references reqd).

II.   MATERIALS AND METHODS

2.1 Materials

The wastewater used for the study was obtained from Dangote Fertilizer Limited, Lekki Free trade zone. The plantain husk (waste from plantain) was collected from Eleko market, Lagos State of Nigeria. Some of the major pieces of equipment used in the study are Spectrophotometer, DR3900 (Hach); Muffle furnace, Gullen-Kamp muffle furnace size 2, GH2000; Mesh Sieve (Tyler series); weighing balance, Adventure OHAUS Corporation; Orbital shaker (Stuart-SSLIS Rotating at 250rpm; Oven (Gullen-KampDHG-9023A); pH Meter (HQ411dPh/mV); Conductivity meter (Cond 3310); Turbidity meter (TL2300(Hach)); Calibrated pipette (Pyrex BS604 made in England)

2.2 Methods

2.2.1 Preparation of Activated Carbon using Plantain Peel

The plantain husk was ripped off to remove dusts and washed with water to remove adhered particles before sun drying for72 hours for easy burning. The dried samples were weighed on an electrical balance in the Chemical Engineering Laboratory at Lagos state University. The dried plantain husk was crushed into smaller sizes and placed into the clay pot, the clay pot was then placed in the muffle furnace at $500^{o}C$ for 1 hour, after which the carbonized plantain husk was sieved to attain 0.5mm before activation. The activation was done by soaking the sieved carbonized plantain husk into a solution of 2M hydrochloric acid following the ratio stated below for 24 hours for activation purpose. The ratio used for the activation was 1:6 by weight;1g of plantain husk with 6g (5ml) for activating agent. The activated plantain husk was removed from the solution and placed in the oven for 2 hours at $60^{o}C$, after which it is then left to cool in a desiccator. After cooling, the plantain husk was washed with distilled/deionized water and placed in a container, ready to be dried in the oven for another 4.5 hours, at $105^{o}C$.

2.2.2 Adsorbent Characterization

2.2.2.1 Moisture Content Determination

Fresh bio-solids weighing 10g was done in Petri dishes that have been cleaned, dried, and pre-weighed. In the dishes, these samples will be thinly distributed. They will be sun-dried for 72 hours and then dried for two hours in an air-circulating oven at 1050 degrees. The dried samples will be weighed to determine constant weight after cooling in a desiccator for 30 minutes. This process will be repeated twice, one hour apart. The percentage moisture content (percent weight loss) was determined in three separate calculations, with the average being used to determine the final value.

$$Moisture\ content(\%) = \frac{Loss\ in\ weight\ in\ drying(g)}{Initial\ sample\ weight(g)} \times 100 \quad \dots\dots\dots\dots\dots\dots\dots(1)$$

2.2.2.2 Bulk Density Determination

Density will be measured on activated sample of 0.5mm and this will be determined by measuring the volume of water displaced when a known weight (2g) of sample of activated carbon is dropped into a graduated measuring cylinder with tapping until the activated carbon fully occupies the cylinder to give a final volume. A $100cm^{3}$ (100ml) calibrated measuring cylinder will be washed and dried, then $50cm^{3}$ (50ml) of the water will be added to the measuring cylinder, 2g of the sample will be transferred into the measuring cylinder and volume of the increased water level (final volume) would be recorded. Care will be taken to ensure that no air bubbles were there before taking volume measurements. The mass and volume will then be recorded and density will be calculated using the equation below.

Volume of water displaced (cm^{3}) = final volume – initial volume

$$Bulk\ density\ (g/cm^{3}) = \frac{Mass\ of\ sample\ (adsorbent)}{Volume\ of\ water\ displaced} \quad \dots\dots\dots\dots\dots\dots\dots\dots\ (2)$$

2.2.2.3 Surface Area Determination

The specific surface area of the activated carbon (plantain husk) will be estimated using sear method (George sear) by agitating 1.5g of activated carbon samples in 100ml of dilute hydrochloric acid at pH of 3. Then a 30g of sodium nitrate (solid) will then be added while stirring the suspension and then the volume make up to 150ml will be done with deionized water. The solution will then be titrated with 0.1N sodium hydroxide (NaOH) to raise the pH from 4 to 9 and the volume V recorded. The surface area according to this method was calculated as:

$$S = 32V - 25 \quad \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\ \dots\dots\ (3)$$

Where;

S is the surface area of the activated carbon,

V is the volume of sodium hydroxide required to raise the pH sample from 4 to 9.

2.2.3 Characterization of the Wastewater

Characterization study of the wastewater gives the description of the distinctive nature or content of the wastewater, which includes pH, COD content, TDS,

TSS, TS, and Turbidity etc. The parameters used to characterize the wastewater are pH, Turbidity of the wastewater, total dissolved solids (TDS) in the wastewater total suspended solids (TSS) in the wastewater, Total organic carbon (TOC) in the wastewater, Chemical oxygen demand (COD) of the wastewater, Biological oxygen demand (BOD) of the wastewater, Total phosphorus, Phosphates, Nitrates, Ammoniacal nitrogen(AN). Standard methods were used for the determination of these parameters for the wastewater samples collected.

2.2.3.1 Measurement of pH

Glass Electrode Principle was used. A calibrated beaker was filled with 100 ml of wastewater as the standard sampling volume. The pH meter was switched on and allowed to warm up for about half an hour. The probe was thoroughly cleaned, adjusted to pH mode, and calibrated in a neutral buffer solution with a pH of 7. The meter was then calibrated for acidic solutions by dipping it into a buffer solution with a pH of 4. Additionally, after putting it in a neutral buffer, submerge it in a pH 9 buffer solution. All excess fluid was removed by shaking the probe before putting it into the wastewater sample to be tested, then measure pH button was pressed so as to take stable readings in two minutes. The pH meters' value was compared with that of the buffer solution then the electrode was placed in the correct buffer solution to take the reading. The electrode was rinsed and dried properly. The dry electrode was placed in the wastewater sample, measure button was pressed and kept for about two minutes to take the actual pH readings.

Equilibrium between electrodes and sample was established by stirring sample to ensure homogeneity and it was stirred gently to minimize carbon dioxide entrainment. For rich buffered samples, the electrode was conditioned after cleaning by dipping them into sample for 1 min, blow-dried and immersed in a fresh portion of the same sample and pH reading was taken. Electrodes were equilibrated by submerging in three or four successive parts of the sample for diluted, inadequately buffered solutions before a fresh sample was collected to determine pH.

2.2.3.2 Determination of Chemical Oxygen Demand (COD)

Open Reflux Method was used. The reflux apparatus used consist of 500 or 250ml Erlenmeyer flasks with ground –glass 24/40 neck and 300 mm jacket Liebig, West or equivalent condenser with 24/40 ground-glass joint and a hot plate having sufficient power to produce at least $1.4 \, W/cm^2$ of heating surface or equivalent. 50ml of wastewater sample was measured using pipette and poured into a 500 ml refluxing flask. 1.0 g $HgSO_4$ and 5.0 ml of sulphuric acid reagent were added with mixing to dissolve $HgSO_4$ Cooling while mixing was done to avoid possible loss of volatile materials. 25 ml of 0.0416 M $K_2Cr_2O_7$ solution was added and mixed thoroughly, flask was then attached to condenser with cooling water flow. The remaining sulphuric acid reagent (70 ml) was added through the open end of the condenser as Continuous swirling and mixing was done while adding sulphuric acid reagent. The condenser's open end was covered with a tiny beaker to keep extraneous objects out of the mixture as it refluxed for two hours. Distilled water was used to cool and clean the condenser.

The reflux condenser was detached, and distilled water was added to thin the liquid to about twice its volume.

The sample was cooled to room temperature and 0.1 to 0.15 ml of ferrous ammonium sulphate (FAS) were used to titrate any excess $K_2Cr_2O_7$ (2 to 3drops). The first sharp color change from bluish green to reddish brown that persists for 1 min or longer was taken as the end point of the titration.

A blank containing the reagents and a volume of distilled water equal to that of sample measured was refluxed and titrated.

COD in sample was calculated using equation (4).

$$\text{COD (mg O}_2\text{/l)} = (A–B) \times M \times 8000 \text{ ml sample} \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots (4)$$

where

A = volume of FAS used for blank (ml)

B = volume of FAS used for sample (ml)

M = molarity of FAS

The whole procedure was also repeated for water samples collected after adsorption process.

2.2.3.3 Determination of Total Solids

To prepare the evaporating dish, a clean dish was heated to 103 or 105^oC for one hour, then it was put away and cooled in a desiccator until it was required. It was weighed before being used. The sample volume was selected to generate between 2.5 and 200 mg of dried residue. If more than 10 minutes are needed to finish the filtration process, the filter's diameter was increased and the sample volume was decreased. A specific volume of thoroughly mixed sample was measured with a pipette and put into a plate that was already weighed. The wastewater sample was pipetted from the approximate midpoint of the container not in the vortex, then a point was chosen at the mid depth and mid-way between wall and vortex. Sample was evaporated to dryness on a steam bath or in a drying oven for at least 1h at 103 to105^oC and then cooled in a desiccator to balance temperature before weighing. Cycle of drying, cooling,

desiccating and weighing until a constant weight was repeated until weight change was less than 4% of previous weight or 0.5mg. When weighing dried sample, exposure to air was avoided to prevent sample degradation.

Total solids (mg) = (A - B) x 1000 Sample volume, ml …………………………………………….. (5)
Where:
A = weight of dried residue + dish (mg)
B = weight of dish (mg)

2.2.3.4 Determination of Total Dissolved Solids
A well -mixed sample is filtered through a standard glass fiber filter and the filtrate is evaporated to dryness in a weighed dish and dried to constant weight at 180^oC. The increase in dish weight represents the total dissolved solid To prepare evaporating dish, the clean dish was heated to 180 ± 2^oC for 1 h in an oven then stored in desiccators until needed. Before use, it was weighed. Sample volume was chosen to yield between 2.5 and 200 mg dried residue. Filter diameter was increased and sample volume decreased if morethan10 min are required to complete filtration.

Sample was stirred with a magnetic stirrer. A measured volume was pipette on to a glass-fiber filter with applied vacuum. Sample was then washed with three successive 10 ml volume of reagent grade water, allowing complete draining between washings and continues suction for 3 min after filtration is complete. Total filtrate with washings was transferred to a weighed evaporating dish and then evaporated to dryness on a steam bath or in a drying oven. The evaporated sample was dried for at least 1 hour at 180°C in an oven, after which the dish was chilled to the proper temperature in a desiccator, and finally it was weighed. Drying, cooling, desiccating, and weighing cycles were repeated until the weight remained constant or the weight change was less than 4% of the initial weight or 0.5mg. When weighing dried sample, exposure to air was avoided to prevent sample degradation. 10% of all samples were analyzed in duplicate and these duplicate determinations were checked if it corresponded with 5% of their average weight. Total solid was calculated using equation (6).

Total dissolved solids mg/L = (A - B) x 1000Samplevolume, ml ………………………………. (6)
Where:
A = weight of dried residue + dish, mg B=weight of dish

2.2.3.5 Determination of Total Suspended Solids
The sample is well mixed then filtered through a weighed standard glass-fibers filter and the residue retained on the filter is dried to constant weight in an oven at 103 to 105^oC. The increase in weight of the filter represents the total solids. To Prepare glass–fiber filter disk, three 20 ml volumes of reagent-grade water were poured into a vacuum and wash disk, and all remaining water and washings were then removed. Filtrate was removed from filtration apparatus and transferred to an inert aluminium weighing dish. Sample placed in the dish was dried in an oven at 103 to 105^oC for 1h and then cooled in a desiccator to balance temperature before weighing. Cycle of drying, cooling, desiccating and weighing was repeated until a constant weight is obtained or until weight change is less than 4% of previous weight or 0.5 mg. This is then stored in desiccator until needed. Sample volume was chosen to yield between 2.5 and 200 mg dried residue. Filter diameter was increased and sample volume decreased if more than10 min are required to complete filtration.

When weighing dried sample, exposure to air was avoided to prevent sample degradation. 10% of all samples were analyzed in duplicate and these duplicate determinations were checked if it corresponded with 5% of their average weight.

Calculation:
mg total solids/l= (A - B) x 1000 Sample volume (ml)
Where:
A = filter weight + dried residue (mg) B= weight of filter

2.2.3.6 Measurement of Turbidity
Nephelometric method was used. First the meter was calibrated after which the sensor was rinsed with distilled water. (30ml) was collected in a clean container and the sample cell was capped. The sample cell was wiped to remove spots and finger prints, then a thin bead of silicone oil was applied from the top to the bottom of the cell. The sample cell was placed in the instrument cell compartment, and the cover of the cell was closed, then the EPA filter was inserted into it. The appropriate ratio, NTU was selected, then after 3seconds the reading was taken. Standard solution was prepared by mixing 5g of fuller's earth previously dried and shifted through 75micron Sieve slowly through constant stirring with distilled water and diluted to1000ml. After being stirred sporadically for an hour, the mixture was

left to stand for 24 hours. Without disturbing the sediment, the supernatant liquid was removed. To calculate the amount of clay in suspension, 50 ml of the extracted liquid was evaporated, and the remainder was dried at 105 + 2°C and weighed. The turbidity standard was prepared with this standardized stock suspension with distilled water and a drop of saturated mercuric chloride solution was added as preservative. The sample was thoroughly shaken before being poured into an appropriate-sized transparent glass bottle (1liter). Then, while holding them against an appropriate background and using a source of light that illuminates them equally and is positioned so that no rays directly reach the eye, it was compared to the turbidity standards contained in comparable bottles. Just before comparison, the standards and the sample were both shaken simultaneously.

2.2.3.7 Measurement of Conductivity

The conductivity meter was first calibrated so as to get accurate results. The probe was soaked into de-ionized water for 30 minutes. Calibration solution was poured into two separate clean containers to a height of 3cm. The meter was switched on and the conductivity mode was selected using the mode button. The probe was rinsed in one of the calibration solution containers by gently stirring the probe. The probe is dipped into the second calibration solution container and tapped at the bottom to remove air bubbles, then it is allowed for 15minutes to stabilize to the solution temperature. The HLD/CAL button on the meter was pressed for 2 seconds so that the conductivity value will be displayed, then take reading. The set button on the meter was pressed so that meter will return to conductivity measurement mode. Sample was taken and the conductivity was measured after which the value was compared to the standard solution measurement. The reading on the display as the conductivity meter automatically select the optimal range. The electrodes were properly cleaned by rinsing in de-ionized water before repeating the process for the different samples.

2.2.3.8 Determination of Ammoniacal Nitrogen Content

Nesslerization method was used. The sample was buffered and distilled. The ammonia in the distillate or in the wastewater sample is treated with Nessler's reagent and the color was developed and matched with that of a series of standard ammonia solutions or measured photometrically at 400 to 425nm. 500ml of water and 20ml of borate buffer solution was added to a distillation flask and pH was adjusted to 9.5 with 6N sodium hydroxide solution, then few glass beads and was added to the mixture to steam out the distillation apparatus until distillate shows no trace of ammonia. 500

ml of dechlorinated sample or a portion diluted to 500 ml with water used was prepared by adding at the time of collection, dechlorinating agent equivalent to chlorine residual contained in the sample. This sample was neutralized to pH 7with dilute acid or alkali and 25 ml of borate buffer was added to adjust pH to 9.5 with 6N sodium hydroxide solution using a pH meter. In order to minimize contamination, the distillation apparatus was left assembled after steaming out until sample distillation process started. The steaming out flask was disconnected and immediately the sample flask was transferred to the distillation apparatus. Sample was distilled at the rate of 6 to 10 ml/minute with the tip of the delivery tube below the surface of acid receiving solution. The distillate was then collected in a 500-ml Erlenmeyer flask containing 50 ml plain boric acid solution for nesslerization method of analysis.

Treatment of undistilled samples: 1 ml zinc sulphate solution was added to 100 ml of sample then 0.4ml to 0.5 ml of 6 N sodium hydroxide solutions was also added to obtain a pH of 10.5 and mixed well. The treated sample was left for a few minutes where upon a heavy flocculent precipitate should fall, leaving a clear and colorless supernate. The sample was clarified by centrifuging or filtering using any filter paper that was pretested to ensure that no ammonia is present.

Color Development

Undistilled samples - 50 ml of sample or a portion diluted to 50 ml with water was used. Since the undistilled portion contains sufficient concentrations of calcium, magnesium or other ions that produce turbidity or precipitate with Nessler reagent, 1 drop (1ml) of EDTA reagent was added and mixed well.

Distilled samples- The pH was raised to the desired high level by adding 2 ml of Nessler's reagent to the boric acid that was used to absorb ammonia distillate. Nessler tubes are capped with spotless rubber stoppers, and the tubes are then inverted at least six times to thoroughly mix the samples. After applying the Nessler reagent, the reaction was allowed to run for at least 10 minutes before the color of the sample and the standards was assessed. The photometry technique was used to measure the color.

Photometric measurement – Then, using a spectrophotometer or filter photometer to measure the absorbance or transmittance, a calibration curve was created using the same temperature and reaction time as the samples. Transmittance data were compared to reagent blanks, and repeated parallel checks were performed using standards in the samples' nitrogen range. Total ammoniacal nitrogen content was also be determined by calculating using the equation (7).

$$\text{Ammoniacal Nitrogen, mg/l(51ml of final volume)} = A \times \frac{B}{V} \times C \dots\dots\dots\dots\dots\dots\dots\dots\dots (7)$$

Where:

A= pg of ammoniacal nitrogen (51ml of final volume);

B = Total volume of distillate collected, in ml, including acid absorbent; C = volume distillate taken for nesslerization, in

ml;

V=volume of sample taken.

The whole procedure was also repeated for water samples collected after adsorption process.

2.2.4 Experimental Design for the Adsorption Process

RSM is a group of mathematical and statistical methods used to optimize the operating conditions for the greatest lead metal ion elimination. The optimal adsorption and reverse osmosis process variables for the removal of COD and ammoniacal nitrogen will next be determined using a three-level, three-factor Box-Behnken factorial design (BBD) (Design Expert Software, Trial Version7.1.6, Stat-ease Inc., Minneapolis, MN, USA).Optimizing a response and establishing a connection between a response (output variable) and the interactive effects of independent factors (input variables) are the basic goals of experimental design (Rao et al., 2015). Understanding and evaluating the impact of various parameters and how they combine to produce the answer is the main benefit of employing RSM (s). Consequently, it is regarded as a suitable strategy to optimize a process with one or more result. The variable input parameters are pH values in the range of 5.5-7.5, contact time of 30-100 seconds and temperature of $25^{o}C$ to $35^{o}C$. The three independent variables were designated as A- pH, B- contact time and C- temperature for the statistical analysis. The low, centre and high levels of each variable are designated as -1, 0, and +1, respectively as illustrated in Table 1.

Table 1: Independent variables and their levels used for Box-Behnken Design.

FACTORS	VARIABLES	LOW LEVEL	CENTER LEVEL	HIGH LEVEL
Temperature (^{o}C)	A	25	30	35
Contact time, (seconds)	B	30	65	100
Ph	C	5.5	6.5	7.5

The experimental levels for each variable were selected based on results from preliminary experiments and coding of the variables was done according to the following equation:

$$xi = \frac{Xi - Xo}{\Delta Xi} \quad \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots(8)$$

Where:

xi is the dimensionless value of an independent variable Xi is the real value of an independent variable

Xo is the real value of an independent variable at the centre point

ΔXi is the step change of the real value of the variable, i, corresponding to the variation of a unit dimensionless value of variable, i.

The number of experiments (N) needed for the development of Box-Behnken matrix is defined as;

$$N = 2K (K-1) + r \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots(9)$$

Where:

K is the factor number is the replicate number of the central point

A total of 17 trials were run in order to optimize the parameter at which the maximum removal was obtained. Executing a statistically designed experiment, estimating the coefficient, analyzing the response, and ensuring the model is appropriate are the three fundamental processes in the optimization process. Selecting the optimal model for expressing the relationship between the response and other influencing independent variables involves conducting investigations using a variety of tests, such as sequential model sum of squares, lack of fit tests, and model summary statistics. To examine the outcome, regression analysis and analysis of variance responses were both used. The most popular second order polynomial equation can be expressed as equation shown below to fit the obtained experimental data and to identify the pertinent model terms;

$$Y = \beta_O + \sum \beta i X i + \sum \beta i i X i i^{2} + \sum \beta i j X i X j + \epsilon \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots (10)$$

Where:

Y is the predicted response (the percentage removal of COD and ammoniacal nitrogen),

β_0 is the constant coefficient,

β_i is the linear coefficient of the input factor X_i

β_{ii} is the ith quadratic coefficient of the input factor X_i

β_{ij} is the different interaction coefficient between the input factor X_i and X_j.

ϵ is the error of the model (Box-Behnken,1960), assumed to have a zero mean.

For this study, the independent variables were coded as A, B and C. Thus, the equation can be represented as equation (11).

$$Y=\beta_0+\beta_i A+\beta_i C+\beta_i C+\beta_{ii} A^2+\beta_{ii} B^2 +\beta_{ii} C^2 +\beta_{ij} AB+\beta_{ij} AC+\beta_{ij} BC \dots\dots\dots (11)$$

2.2.4.1 Desirability Function

The desirability function approach is a technique for the simultaneous determination of optimum settings of input variables that can determine optimum performance levels for one or more responses. The desirability procedure involves two steps:

- Finding the levels of the independent variables that simultaneously produce the most
- Maximize the overall desirability with respect to the controllable factors.

The desirability function approach was originally introduced by Harrington, 1965. Then another version was developed by Derringer and Suich (1980). The general approach is to first convert each response (Y_i)into an individual desirability function (d_i) varying over the range

$$0 \le d_i \le 1$$

Where if response Y_i is at its goal or target, then $d_i=1$, if the response is outside an acceptable region, $d_i=0$.Then the design variables are chosen to maximize the overall desirability.

$$D = (d_1 \times d_2 \times \dots \times d_n)^{1/n} \dots\dots\dots (12)$$

Where n is the number of responses in the mixture.

2.2.5 Adsorption Experiment

First the materials used for sample preparation were thoroughly washed with liquid soap and deionized water. Then the containers were dried at ambient temperature till they were completely dry. The batch adsorption experiments was carried out on the removal of COD and ammoniacal nitrogen from industrial wastewater to study the effect of some specific process parameter.

In the kinetic experiments, the parametric effects of temperature, contact time, and initial Ph will be investigated for the adsorption onto plantain husk. 250 ml of wastewater with pH range of (5.5 to 7.5) will be transferred into a 500ml conical flask and each solution agitated at 250rpm in an orbital shaker over a temperature range of (25^oC to 35^oC) and contacted for a period of 30seconds to 100seconds. At the end of each contact time, the solution will be filtered using Whatmann No. 1 filter paper and the residual concentrations analyzed. The pH of the solution will be adjusted using hydrochloric acid and sodium hydroxide. The concentrations of COD and ammoniacal nitrogen in the filtrate will be analyzed using the spectrophotometer. Batch adsorption experiments will be carried out at the above temperature range by shaking series of beakers containing the desired pH in a known concentration wastewater. Samples of the wastewater will then be withdrawn at different intervals, filtered and the filtrate analyzed for the trace of COD and ammoniacal nitrogen content. The design of this experiment was done using Box-Behnken Design method of response surface analysis which specifically made each effect to require only three (3) levels given in table below. Then the concentrations of the samples will be determined by using a calibrated curve.

The removal efficiency of COD and ammoniacal nitrogen was defined as:

$$Re (\%) = \frac{c_i - c_f}{c_i} \times 100 \dots\dots\dots (13)$$

Where;

Re (%) was the ratio of difference in COD/ammoniacal nitrogen concentration before and after adsorption.

C_i was the concentration of COD/ammoniacal nitrogen before adsorption (mg/l)

C_f as the concentration of COD/ammoniacal nitrogen after adsorption(mg/l)

The amount of COD/ammoniacal nitrogen adsorbed at time t, (q_t) was calculated using the formula above.

$$q_t = \frac{C_i - C_f}{C_i} \quad X \quad V \dots\dots\dots (14)$$

Where;

V was the volume (L) of the wastewater used for adsorption. M was the mass (g) of the adsorbent used.

Basis: 500ml of wastewater and 2g of adsorbent will be used for the adsorption studies.

III. RESULTS

The results of the characterization of the wastewater before treatment is shown in Table 2, while the results of the characterization of the plantain husk adsorbent is shown in Table 3. The moisture content was 22.5%, bulk density was 497g/L and surface area was $967m^2/g$. The bulk density determines the mass of adsorbent in specific volume and it was calculated as $0.497g/cm^3$. The sieving of the grounded plantain husk was also analyzed using mesh sieve of 0.5mm.

Table 2: General Characterization of Wastewater Before the Adsorption Experiment

Constituents	Value	Unit
Ph	6.0	-
Turbidity	1.4	NTU
Total dissolved solids (TDS)	326	Mg/l
Total suspended solids (TSS)	3.6	Mg/l
Total organic carbon (TOC)	0.1	Mg/l
Chemical oxygen demand (COD)	412	Mg/l
Total phosphate	0.72	Mg/l
Nitrates	1.5	Mg/l
Biological oxygen demand (BOD)	5.2	Mg/l
Conductivity	501	S/m
Ammoniacal nitrogen	86	Mg/l
Copper (Cu)	0.8	Mg/l
Zinc (Zn)	0.5	Mg/l
Iron (Fe)	0.1	Mg/l

Table 3: Physiochemical Characteristics of Adsorbent

Parameter	Value	Unit
Moisture content	22.5	%
Bulk density	0.497	g/cm^3
Surface area	967	m^2/g

3.1 Box-Behnken Statistical Analysis

After the experiment, the initial and final concentration of the pollutants were used to calculate the percentage removal of the pollutants and the percentage removal were recorded as the responses into the Box Behnken design so as to obtain the optimum conditions of the various parameters considered.

The Box-Behnken responses were analyzed and the results for Adsorption experiment of COD and ammoniacal nitrogen is presented in Table 4.

Table 4: Experimental Box-Benhken Design with Responses for adsorption

Std	Run	Block	Factor 1 Temperature (Oc)	Factor 2 Contact Time	Factor3 Ph	Response 1 % Cod Removal (%)	Response 2 % Ammoniacal Nitrogen Removal (%)
8	1	Block1	35	65	7.5	87	90
15	2	Block1	30	65	6.5	85.1	99.1
12	3	Block1	30	100	7.5	82	88
14	4	Block1	30	65	6.5	87.8	98.8
10	5	Block1	30	100	5.5	84.65	96.65
5	6	Block1	25	65	5.5	85.5	91.5
7	7	Block1	25	65	7.5	80	92
9	8	Block1	30	30	5.5	77.5	92.5
3	9	Block1	25	100	6.5	98.2	97.75
16	10	Block1	30	65	6.5	85.8	99.8
13	11	Block1	30	65	6.5	85.4	98.4
1	12	Block1	25	30	6.5	85.02	99.02
6	13	Block1	35	65	5.5	75.3	92.3
4	14	Block1	35	100	6.5	89.79	96.79
17	15	Block1	30	65	6.5	85	99
11	16	Block1	30	30	7.5	83.8	98.8
2	17	Block1	35	30	6.5	95.9	98.9

As established earlier from the literature, the response of COD and Ammoniacal nitrogen removal via adsorption depends on certain factors and this factor includes the parameters which act as conditions to the process. In this study, the combined effect of these parameters on COD and Ammoniacal Nitrogen removal were investigated and optimized. Optimization by classical method involving one factor at a time (OFAT) is time consuming and expensive. Besides this, number of trials required will be large, making the full factorial design very complex.

3.2 COD and Ammoniacal Nitrogen Response

In order to overcome such difficulties experimental Box-Behnken design was used for optimization of the various parameters for COD and ammoniacal nitrogen removal. Parameters and their corresponding range considered are temperature (25°C to 35°C), contact time (30 to 100 seconds), and pH of (5.5 to 7.5). The experiments were conducted at different level of combination of these parameters using statistically designed experimental procedure. The coded and actual values of the independent variables A (temperature), B (contact time), and C (pH) as designed by design expert 7.0.0 with their corresponding response (predicted and actual) is showed in Tables 5.

The Coded values stated above is the minimum, centre and maximum values of the three parameters (temperature, pH, contact time) which was varied in this adsorption experiment. The number (-1) is for the minimum value, (0) is for the centre value and (1) is for the maximum value. The predicted values in the table above is the standard reference for the adsorption experiment when carried out under standard conditions by varying those three parameters while the actual values are the values gotten by carrying out this experiment.

Regression Model Equation for COD and Ammoniacal Nitrogen Concentration after Adsorption Experiment

A system or process with several variables is likely to be influenced by several external as well as internal parameters and low order interactions. Investigations on linear, cubic, two factor interaction and quadratic model were done to select the statistically significant model for determining the relationship between the response and input (independent variables).

For the adsorption experiment, it can be seen that p value for the sequential model sum of squares is less than 0.0001 for both COD and Ammoniacal Nitrogen and F value for COD is (37.06) while that of Ammoniacal Nitrogen is (75.55) for quadratic model (Tables 8 and 9). Lack of fit test for quadratic model was found to be insignificant for both the COD and Ammoniacal Nitrogen which indicates that the model fits the experiment and its p value was 0.3868 for COD and 0.2949 for Ammoniacal Nitrogen.

From the model summary statistics (Tables 6 and 7), it can be predicted that the quadratic model had maximum predicted and adjusted R^2 value. From the above results, it had been concluded that quadratic model provides an excellent relationship between the response and the independent variables.

Table 5: The Box-Behnken Design and the Adsorption Experimental Response of Dependent Variable Y (COD and Ammoniacal Nitrogen Concentration, mg/L)

Runs	Factors						Responses		Responses	
	Coded Levels			Actual Values			COD Concentration		Ammoniacal Nitrogen Concentration	
	A	B	C	A	B	C	ACTUAL	PREDICTED	ACTUAL	PREDICTED
1	1	0	1	35	65	7.5	87	87.39	90.00	89.95
2	0	0	0	30	65	6.5	85.1	85.82	99.10	99.02
3	0	1	1	30	100	7.5	82	82.53	88.00	88.48
4	0	0	0	30	65	6.5	87.8	85.82	98.80	99.02
5	0	1	-1	30	100	5.5	84.6	84.54	96.65	96.99
6	-1	0	-1	25	65	5.5	85.5	85.11	91.50	91.55
7	-1	0	1	5	5	7.5	80	78.97	92.00	91.92
8	0	-1	-1	30	30	5.5	77.5	76.96	92.50	92.02
9	-1	1	0	25	100	6.5	98.2	98.69	97.75	97.36
10	0	0	0	30	65	6.5	85.8	85.82	99.80	99.02
11	0	0	0	30	65	6.5	85.4	85.82	98.40	99.02
12	-1	0	0	25	30	6.5	85.02	85.94	99.02	99.44
13	1	0	1	35	65	5.5	75.3	76.32	92.30	92.38
14	1	1	0	35	100	6.5	89.7	88.86	96.79	96.37
15	0	0	0	30	65	6.5	85	85.82	99.00	99.02
16	0	-1	1	30	30	7.5	83.8	83.90	98.80	98.46
17	1	1	0	35	30	6.5	95.9	95.40	98.90	99.29

From the Tables 6 and 7 above, the coefficient of determination (R^2) of the model were 0.9794(COD) and 0.9898 (Ammoniacal Nitrogen) which indicated a good fit between predicted values and the experimental data points. In addition, this implies that 97.94% and 98.98% of the variations for percent COD and Ammoniacal Nitrogen adsorption experiment are explained by the independent variables, and this also

means that model does not explain only about 2.06% and 1.02% of variation respectively. Predicted R^2 is a measure of how good the model predicts a response value. Experiments were performed using the Box-Behnken experimental design. The experimental and predicted COD and Ammoniacal Nitrogen concentrations are shown along with the experimental conditions in Table 5. Based on the model analysis, a quadratic model was chosen to fit the data.

Table 6: Model Summary Statistics for COD Response in the Adsorption experiment

Source	Std. Dev.	R-Squared	Adjusted R-Squared	Predicted R-Squared	PRESS	
Linear	6.07	0.0617	-0.1549	-0.9533	996.72	
2FI	5.40	0.4282	0.0851	-1.8927	1476.12	
Quadratic	**1.22**	**0.9794**	**0.9530**	**0.8207**	**91.48**	**Suggested**
Cubic	1.15	0.9896	0.9585	N/A	N/A	Aliased

Table 7: Model Summary Statistics for Ammoniacal Nitrogen Response in the adsorption experiment

Source	Std. Dev.	R-Squared	Adjusted R-Squared	Predicted R-Squared	PRESS	
Linear	4.14	0.0646	-0.1512	-0.7490	416.07	
2FI	4.06	0.3085	-0.1064	-1.6840	638.51	
Quadratic	**0.5885**	**0.9898**	**0.9767**	**0.9006**	**23.66**	**Suggested**
Cubic	0.5119	0.9956	0.9824	N/A	N/A	Aliased

3.3 Analysis of Variance (ANOVA)

Analysis of variance, ANOVA, is a statistical decision-making tool used for detecting any differences in average performances of tested parameters (Motjaba et al., 2016). It employs sum of squares and F statistics to find out relative importance of the analyzed processing parameters, measurement errors and uncontrolled parameters. Analysis of variance (ANOVA) was used to check the adequacy of the model for the responses in the experimentation. It subdivides the total variation of the results in two sources of variation, the model and the experimental error, showing whether the variation from the model is significant when compared to the variation due to residual error (Mojtaba et al., 2016). Fisher's F-test value, which is the ratio between the mean square of the model and the residual error, performs this comparison (Kasiri et al., 2013).

Response Surface Quadratic Model of COD and Ammoniacal Nitrogen

Table 8: Analysis of Variance for COD after Adsorption experiment

Source	Sum of squares	Degree of freedom	Mean square	F value	P value prob>F	
Model	499.79	9	55.53	37.06	<0.0001	Significant
A Temperature	0.0666	1	0.0666	0.0445	0.8390	
B-contact time	19.28	1	19.28	12.87	0.0089	
C- pH	12.13	1	12.13	8.09	0.0249	
AB	93.03	1	93.03	62.08	0.0001	
AC	73.96	1	73.96	49.36	0.0002	
BC	20.03	1	20.03	13.36	0.0081	
A^2	42.71	1	42.71	28.50	0.0011	
B^2	43.72	1	43.72	29.18	0.0010	
C^2	209.57	1	209.57	139.86	<0.0001	
Residual	10.49	7	1.50			
Lack of fit	5.20	3	1.73	1.31	0.3868	Not significant
Pure Error	5.29	4	1.32			
Cor Total	510.28	16				

Table 9: Analysis of Variance for Ammoniacal Nitrogen after Adsorption experiment

Source	Sum of squares	Degree of freedom	Mean square	F value	P value prob>F	
Model	235.47	9	26.16	75.55	< 0.0001	significant
A-Temperature	0.6498	1	0.6498	1.88	0.2131	
B- Contact time	12.58	1	12.58	36.31	0.0005	
C- pH	2.15	1	2.15	6.22	0.0414	
AB	0.1764	1	0.1764	0.5094	0.4985	
AC	1.96	1	1.96	5.66	0.0490	
BC	55.88	1	55.88	161.34	< 0.0001	
A^2	12.47	1	12.47	36.02	0.0005	
B^2	2.81	1	2.81	8.10	0.0248	
C^2	144.03	1	144.03	415.90	< 0.0001	
Residual	2.42	7	0.3463			
Lack of fit	1.38	3	0.4587	1.75	0.2949	not significant
Pure Error	1.05	4	0.2620			
Cor Total	237.89	16				

Table 10: Statistical Information on Box-Behnken Design for COD removal by Adsorption

Std Dev.	1.22	R-Squared	0.9794
Mean	85.52	Adj R- Squared	0.9530
C.V%	1.43	Pred. R- Squared	0.8207
PRESS	91.48	Adequate precision	23.8229

Table 11: Statistical Information on Box-Behnken Design for Ammoniacal Nitrogen removal by Adsorption

Std Dev.	0.5885	R-Squared	0.9898
Mean	95.84	Adj R- Squared	0.9767
C.V%	0.6140	Pred. R- Squared	0.9006
PRESS	23.66	Adequate precision	24.2966

The coefficient of Variance (CV) is the ratio of standard error of estimation to the mean value and it is considered reproducible once it is less than 10%. In this study, CV obtained for COD and Ammoniacal nitrogen removal by adsorption were 1.43% and 0.6140% respectively. Adequate precision value measures signal to noise ratio and a ratio greater than 4 is desirable. The obtained ratios from the study were 23.8229 and 24.2966 for COD and ammoniacal nitrogen respectively for the adsorption experiment which indicate an adequate signal.

3.4 Estimation of Quantitative Effects of the Factors That Affects % COD Removal by Adsorption

From the Figure 1, it was deduced that as both contact time (from 30 to 100 seconds) and temperature (25 to 35°C) increased, COD removal also increased from 75% to 97%. This can be traced back to effect of time on rate of adsorption since increasing time of contact between the adsorbent and the adsorbate increases the rate of adsorption and this implies that the active site is well filled with dissolved oxygen if contacted for a long. Also, as the temperature increases the dissolved oxygen molecules (COD) migrates rapidly from the bulk of the wastewater phase to the surface of the adsorbent which is because the intermolecular forces binding the dissolved oxygen to the wastewater are distorted at elevated temperatures.

Research by (Milon et al., 2015) has shown that COD removal is higher at pH = 7 (neutral) which conforms with the findings shown in Figure 2. Also, from the graph, it can be deduced that there is a slight decrease in COD removal from 83% to 79% at pH =7.5 (alkaline medium) as compared to the drastic decrease in COD removal from 83% to 70% at pH =5.5 (acidic medium). This is due to the fact that the active sites of the adsorbent used are acidic and it is positively charged so it will favour an alkaline medium than the acidic medium because the alkaline medium is negatively charged. Also, COD removal decreased initially from 75% to 70% as the temperature increased from 25°C to 31°C called the **trough point** (at 31°C) where further increase in the temperature from 31°C to 35°C shows minimal increase in the percentage removal of COD from 70% to 73%. Hitherto, effect of temperature on COD removal is a direct correlation but from the graph shown in fig 4.2b above, increase in temperature led to the decrease in COD removal and this is because the pH parameter has a more significant effect on COD removal than temperature.
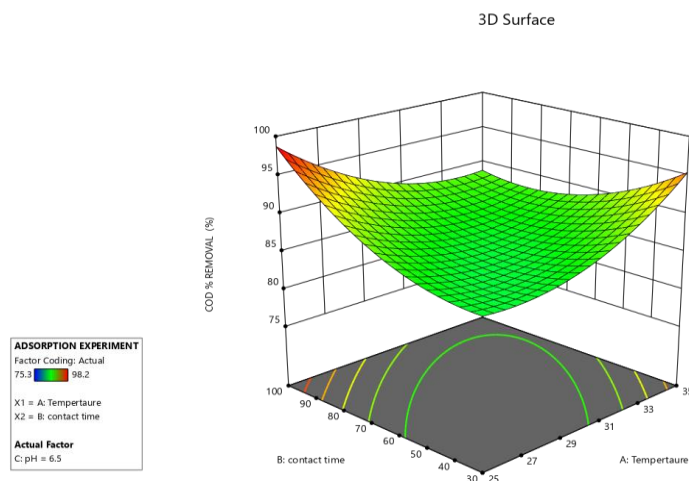
Figure 1: Surface plot of the predicted COD percentage removal by adsorption as a function of Temperature and contact time with pH fixed at 6.5
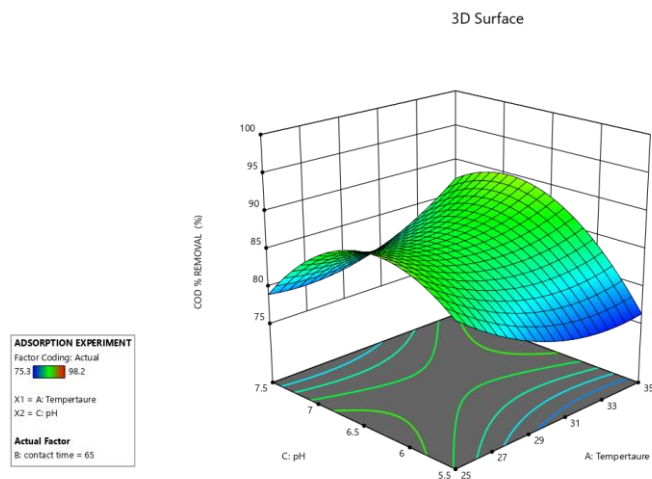

Figure 2: Surface plot of the predicted COD percentage removal by adsorption as a function of Temperature and pH with contact time fixed at 65 seconds

From Figure 3 it is observed for contact time, percentage COD removal increases from 69%to 85% and this corresponds to lower contact time value (30seconds) to a contact time higher value (100seconds). As said earlier, this can be traced back to effect of time on rate of adsorption since increasing time of contact between the adsorbent and the adsorbate increases the rate of adsorption and this implies that the active site is well filled with dissolved oxygen if contacted for a long. Also, it can be seen from the graph that at pH of 7(neutral) there is maximum COD removal of 85%

which also conforms to the findings from various researchers but as pH increased to 7.5(alkaline), there was a slight decrease in the COD removal percentage to 83% as compared to the drastic decrease in COD removal percentage to 69% as pH of 5.5 (acidic). As earlier said, it is due to the fact that the active sites of the adsorbent used are acidic and it is positively charged so it will favour an alkaline medium than the acidic medium because the alkaline medium is negatively charged.
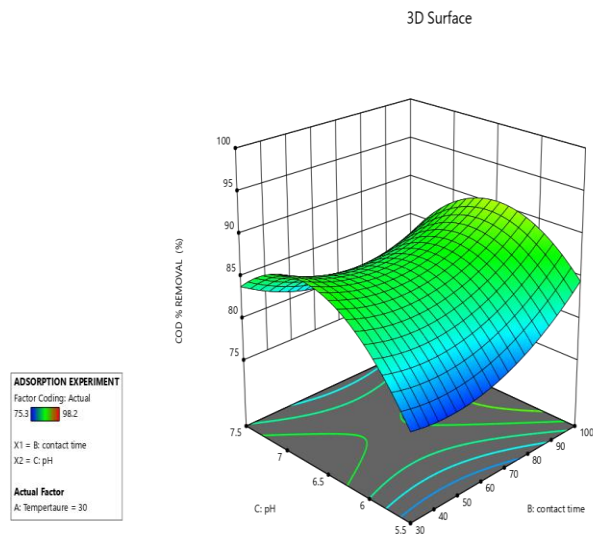
Figure 3: Surface plot of the predicted COD percentage removal by adsorption as a function of contact time and pH with temperature fixed at 30°C

Estimation of Quantitative Effects of the Factors that Affects % Ammoniacal Nitrogen Removal by Adsorption

From the Figure 4, it was observed that as both contact time and temperature increases, Ammoniacal nitrogen concentration in the wastewater decreases leading to percent increase in Ammoniacal nitrogen removal. This can be traced back to effect of time on rate of adsorption since increasing time of contact between the adsorbent and the adsorbate increases the rate of adsorption it implies that the active site is well filled

with Ammoniacal nitrogen if contacted for long. Also, temperature increase, increases the rate of Ammoniacal nitrogen removal in the sense that as the temperature increases the dissolved Ammoniacal nitrogen molecules migrates rapidly from the bulk of the wastewater phase to the surface of the adsorbent which is because the intermolecular forces binding the A-N molecules to the wastewater is distorted at elevated temperatures. Therefore, it can be concluded that the interaction between both factors have an overall positive effect on removal of Ammoniacal nitrogen by adsorption process.
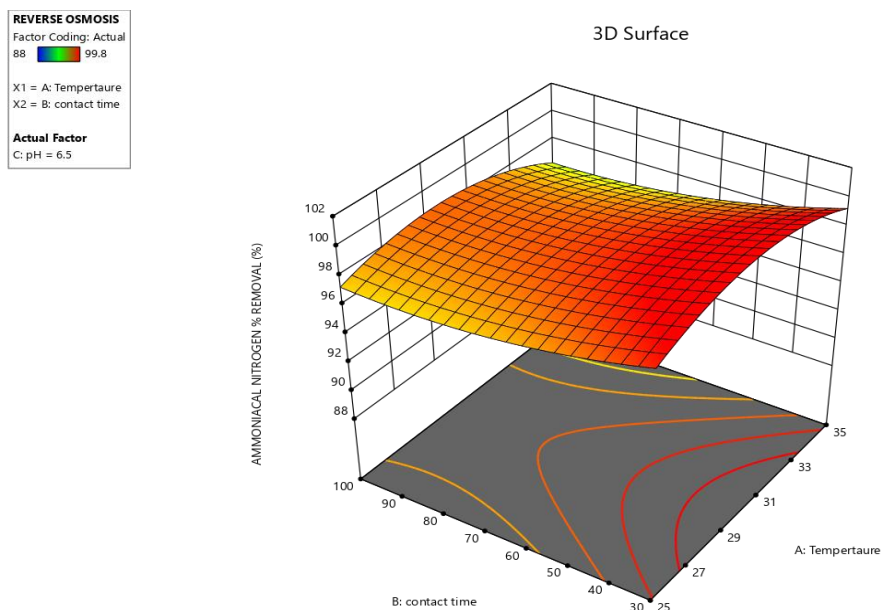

Figure 4: Surface plot of the predicted Ammoniacal Nitrogen percentage removal by Adsorption as a function of Temperature and contact time with pH fixed at 6.5

From Figure 5, it can be deduced that temperature increases from a low value of (25ºC) and high value of (35 ºC), percentage Ammoniacal nitrogen removal also increases from 70% to 93%. This is reasonable because research has shown that increased temperature increases the rate of adsorption. Also, at pH of 7(neutral) Ammoniacal nitrogen removal was maximum at a value of 94% which also conforms to the findings from various researchers but as pH increased to 7.5 (alkaline), there was a slight decrease in the Ammoniacal nitrogen removal percentage to 92% as compared to the drastic decrease in Ammoniacal nitrogen removal percentage to 70% as pH of 5.5 (acidic). As earlier said, it is due to the fact that the active sites of the adsorbent used are acidic and it is positively charged so it will favour an alkaline medium than the acidic medium because the alkaline medium is negatively charged.

From Figure 6, it was observed that as contact time increases from 30 seconds to 100seconds, percentage Ammoniacal nitrogen removal increases from 90 %to 97% which conforms with the effect of time on rate of adsorption since increasing time of contact between the adsorbent and the adsorbate increases the rate of adsorption which can also meant increase in Ammoniacal nitrogen removal because the active site of the adsorbent is well filled with Ammoniacal nitrogen if contacted for long. Also, it can be seen that at pH of 7(neutral), Ammoniacal nitrogen percentage removal has a high value of 99% but as pH increased to 7.5(alkaline), there was a slight decrease in Ammoniacal nitrogen removal from 99% to 98% as compared to the drastic decrease in Ammoniacal nitrogen removal percentage from 99% to 73% at pH of 5.5 (acidic).
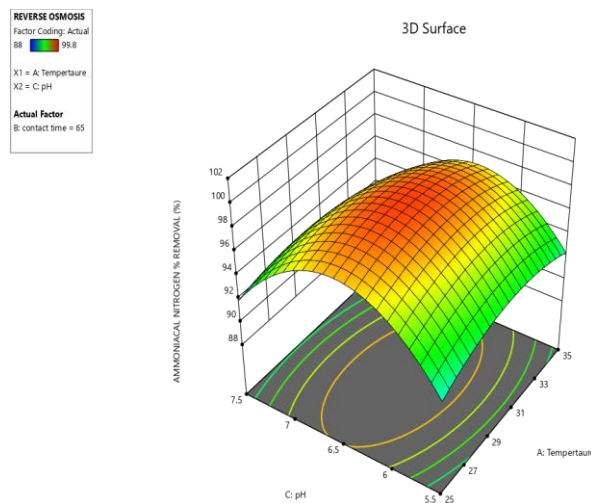

Figure 5: Surface plot of the predicted Ammoniacal Nitrogen percentage removal by adsorption as a function of Temperature and pH with contact time fixed at 65 seconds
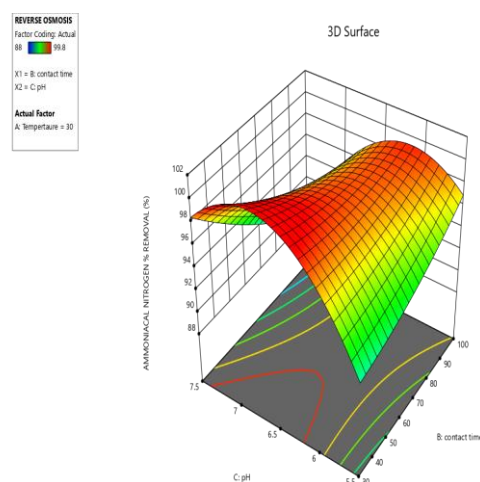

Figure 6: Surface plot of the predicted Ammoniacal Nitrogen percentage removal by adsorption as a function of contact time and pH with temperature fixed at 30ºC

IV. CONCLUSION

The use of plantain husk in removal of ammoniacal nitrogen and chemical oxygen demand (COD) from petrochemical wastewater was investigated. It can be concluded that the interaction between contact time and pH as compared to other interactions has an overall positive effect in the adsorption process of Ammoniacal nitrogen from wastewater. Ammoniacal nitrogen removal with plantain husk adsorbent was about 93% maximum and as pH increased to 7.5 (alkaline), a slight decrease in the Ammoniacal nitrogen removal percentage to about 92% could be attained. Furthermore, percentage removal of COD from the wastewater of about 83% maximum could be obtained. Effect of temperature on COD removal is a direct correlation as increase in temperature could lead to the decrease in COD removal. However, pH parameter has a more significant effect on COD removal than temperature while using the plantain husk as the adsorbent.

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