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Removal of COD And Ammoniacal-Nitrogen from Industrial Wastewater Using Reverse Osmosis

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ABSTRACT: Wastewater from Dangote Fertilizer Limited (DFL) was treated using reverse osmosis with consideration of the factors (pH, temperature and contact time) that impedes the efficiency of the method. 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 waste water samples were characterized before and after the treatment using standard methods to determine Chemical oxygen demand (COD), Ammoniacal nitrogen (AN) and other necessary parameters. From the results obtained optimum temperature for removal of COD by reverse osmosis in this study was 33ºC while optimum temperature for removal of AN was 29ºC. AN removal with reverse osmosis was about 91% maximum. As pH increased to 7.0 from 5.5 there was increase in AN removal from 68% to 78% and the percentage removal of COD increases from 75% to 81% which conforms the fact that the COD removal is favored in moderate acidic medium environment. Also, the increase in contact time from 30 to 100seconds led to the increase in percentage removal of AN from 68% to 91% and favors the COD percentage removal as it increases from 75% to 86%.

KEYWORDS: Ammoniacal nitrogen, Chemical oxygen demand (COD), reverse osmosis,

I. INTRODUCTION

In the petroleum and petrochemical industries worldwide, water is used extensively for various industrial operations, which include employing it as a reactant, solvent, cleaning/stripping agent, steam production, cooling, and boiler water. These needs are satisfied utilizing the few freshwater resources, including groundwater, surface water, ocean, and recycled water, resulting in wastewater that can be hazardous to the environment, if not treated. Wastewater released into the environment by these industries continued to raise serious concerns and causing a number of environmental hazards due to the several pollutants therein, including the biggest polluters of water sources in the environment: ammonia, hydrogen sulfide, mercury, arsenic, etc. Hence, it is very important to find a way of reducing water use and treating wastewater to make it reusable and less hazardous (Breida et al., 2019). The released wastewater contains a small number of pollutants that are classified as volatile organic compounds (VOCs), nutrients, refractory organics, heavy metals, and physical and chemical contaminants. Characteristics of wastewater are frequently defined in terms of Total Organic Carbon (TOC), and Total Suspended Solids (TSS), Biochemical Oxygen Demand (BOD) and BOD5, Chemical Oxygen Demand (COD). The test of COD, which quantity of oxygen needed to oxidize both organic and inorganic molecules in water, 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. Typically, COD levels in wastewater discharged from fertilizer factories range from 111.36 to 293.12 mg/l, making it harmful to the environment and necessitating treatment. Furthermore, wastewater 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).

Several methods have been investigated in treatment of wastewaters and reverse osmosis is one of the methods that had attracted the interest of researchers. Though RO is just one of the options when it comes to managing and treating wastewater, due to the many benefits, it's becoming an increasingly popular choice in manufacturing processes. Reverse osmosis (RO) is a known technique that ensures correct treatment of the wastewater, making it a valuable application in the use of wastewater streams. RO is used to improve water quality by removing salts and pollutants from

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the water (Garud et al., 2011). In the reverse osmosis process, water travels through a semi-permeable membrane that filters out organic matter including ammoniacal nitrogen, COD, and BOD as well as inorganic minerals like calcium, magnesium, potassium, fluoride, salt, and phosphorus. Additionally, some organic chemicals, such as some pesticides are also removed (Das et al., 2020). RO can be used to remove naturally occurring arsenic, which can contaminate groundwater and has become a major issue with water quality in many regions of the world (Das et al., 2020). Reverse osmosis units are frequently used in conjunction with mechanical filters and activated carbon filters. When this happens, the water first goes through the mechanical filter to get rid of sand and other large particles, then the reverse osmosis unit, and finally the activated carbon filter to get rid of any remaining organic compounds (Das et al., 2020). Reverse osmosis permeate flux depends on whether a process is exothermic or endothermic, hence temperature could be considered as one of the factors that can affect the efficiency of reverse osmosis in wastewater treatment. In this study, impacts of some factors like temperature, contact time, etc on the usage of reverse osmosis to treat wastewater from fertilizer industries was investigated.

II. METHODOLOGY

A Materials

Wastewater obtained from Dangote Fertilizer Limited, Lekki Free trade zone was used for the study. 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); Single Reverse Osmosis Skid (MODEL) by Lubron water Technologies (UK)

B Methods

B.1 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. The procedures employed by Akinyemi and Nkemdilim (2022) for determination of the these properties of wastewater samples before and afeter reverse osmosis process were used in this study. To determine the pH of the wastewater samples Glass Electrode Principle was used while Open Reflux Method was used for COD determination as described by Akinyemi and Nkemdilim (2022). Also, for the TS, TDS and TSS, the methods described by Akinyemi and Nkemdilim (2022) were used. Furthermore, Nephelometric method described Akinyemi and Nkemdilim (2022) was used for the determination of turbidity of the wastewater samples, while Nesslerization method was used for the determination of the ammoniacal Nitrogen content of the wastewater samples. The conductivity meter was used to determine the conductivity of the wastewater samples.

B.2 Experimental Design for The Reverse Osmosis

Response Surface Methodology (RSM) is a group of mathematical and statistical methods used to optimize the operating conditions for the greatest lead metal ion elimination. The optimal reverse osmosis process variables for the removal of COD and ammoniacal nitrogen was 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). According to Rao et al., (2015), 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. The main benefit of employing RSM (s) is understanding and evaluating the impact of various parameters and how they combine to produce the answer. Therefore, RSM is regarded as a suitable strategy to optimize a process with one or more result. The variable input parameters used in this study were pH values in the range of 5.5-7.5, contact time of 30-100 seconds and temperature of 25°C to 35°C. The three independent variables were designated as A for pH, B for contact time and C for temperature for the statistical

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analysis. The high, centre and low levels of each variable were 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	HIGH LEVEL (+1)	CENTER LEVEL (0)	LOW LEVEL (-1)
Temperature (ºC)	A	35	30	25
Contact time, (seconds)	B	100	65	30
pH	C	7.5	6.5	5.5

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

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

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 was defined as;

$$N= 2K (K-1) + r \quad ....(1)$$

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;

$$Y= \beta_O + \sum \beta iXi + \sum \beta iiXii^2 + \sum \beta ijXiXj + \epsilon \quad ....(2)$$

Where:

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

β_O is the constant coefficient,

β_i is the linear coefficient of the input factor X_i

β_{ii} is the i^{th} 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 assumed to have a zero mean (Box-Behnken, 1960)

In this study, the independent variables were coded as A, B and C. Thus, the equation can be represented as equation 3.

$$Y=\beta_0+\beta_i A+\beta_i C+\beta_i C+\beta_{ii} A^2+\beta_{ii} B^2 +\beta_{ii} C^2 +\beta_{ij} AB+\beta_{ij} AC+\beta_{ij} BC \quad .... (3)$$

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B.2.1 Desirability Function

The technique for the simultaneous determination of optimum settings of input variables that can determine optimum performance levels for one or more responses is known as desirability function approach. The procedure for the technique 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 general approach is to first convert each response (Yi) into an individual desirability function (di) varying over the range

$$0 \leq d_i \leq 1 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (4)$$

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

$$D = (d1 \times d2 \times \ldots . \times d_n)^{1/n} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (5)$$

Where n is the number of responses in the mixture.

B.3 Reverse Osmosis Experiment

The reverse osmosis (RO) experiments was carried out in batch on the removal of COD and ammoniacal nitrogen from industrial wastewater to study the effect of some specific process parameter using a single reverse osmosis skid (Figure 1). In the kinetic experiments, the parametric effects of temperature, contact time, and pH were investigated for the removal of COD and ammoniacal nitrogen by passing the wastewater through a single reverse osmosis skid that contains separation membranes.1000mlofwastewater with pH range of (5.5 to 7.5) and temperature range of (25ºC to 35ºC) was transferred into a small-sized feed tank connected to the suction of a small pump with suction pressure of 1.5kg/cm^2 and discharge pressure of 4kg/cm^2. The wastewater sample was pumped from the feed tank into the RO skid and then allowed to stay for the stipulated period of time before the discharge valve was opened and the treated water sample was collected with a container placed below the discharge line. The discharge valve was then closed and the process is repeated for a period of 30 to 100 seconds. At the end of each contact time, the solution was poured into the sample bottles 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 treated water were analyzed using the spectrophotometer. Batch reverse osmosis experiments was carried out at the temperature range (25ºC to 35ºC) by shaking series of beakers containing the desired pH in a known concentration wastewater. Samples of the wastewater were withdrawn at different intervals, from the skid and 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 1. 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:

$$Re(\%) = \frac{Cf - Cp}{Cf} \times 100 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (6)$$

Where;

Re (%) was the ratio of difference in COD/ammoniacal nitrogen concentration before and after the reverse osmosis experiment.
C_f is the COD/ammoniacal nitrogen concentration in the wastewater before the reverse osmosis experiment (mg/L)
C_p is the concentration of COD/ammoniacal nitrogen in the permeate (wastewater) after the reverse osmosis experiment (mg/l)
To know the amount of COD/ammoniacal nitrogen removed at those time intervals, the concentration of COD and ammoniacal nitrogen in the reject or concentrate can be analyzed. Figure 1 shows the single reverse osmosis skid used to carry out the reverse osmosis experiment.

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Figure 1. Image of a single reverse osmosis skid

III. RESULTS

The results of the characterization of the wastewater before treatment is shown in Table 2. The turbidity was 1.4NTU while the pH obtained was 6.0. Values obtained for other parameters like TSS to zinc composition are as shown in the table.

Table 2 Characterization of Wastewater before the Reverse Osmosis Experiment

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

A 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 reverse osmosis

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Std	Run	Block	Factor1 Temperature (^{O}c)	Factor 2 Contact Time (Minutes)	Factor3 PH	Response 1 % Cod Removal (%)	Response 2 % Ammoniacal Nitrogen Removal (%)
13	1	Block1	30	65	6.5	87	87.4
16	2	Block1	30	65	6.5	87.4	85
15	3	Block1	30	65	6.5	87.9	84
17	4	Block1	30	65	6.5	87.8	82
7	5	Block1	25	65	7.5	84	82.2
10	6	Block1	30	100	5.5	85.5	90
3	7	Block1	25	100	6.5	80	82
8	8	Block1	35	65	7.5	77.5	74
11	9	Block1	30	30	7.5	81	80
6	10	Block1	35	65	5.5	85	86
5	11	Block1	25	65	5.5	85.4	86.95
9	12	Block1	30	30	5.5	86.02	85.7
2	13	Block1	35	30	6.5	75.3	71
12	14	Block1	30	100	7.5	82	83.8
1	15	Block1	25	30	6.5	85	83
4	16	Block1	35	100	6.5	83.8	84.8
14	17	Block1	30	65	6.5	87	86

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.

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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.

B. 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.

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

Runs	Factors						Responses COD Percentage Removal		Responses Ammoniacal Nitrogen Percentage Removal	
	CODED LEVELS			ACTUAL VALUES			(%)		(%)	
	A	B	C	A	B	C	ACTUAL	PREDICTED	ACTUAL	PREDICTED
1	0	0	0	30	65	6.5	87	87.42	87.4	84.88
2	0	0	0	30	65	6.5	87.4	87.42	85	84.88
3	0	0	0	30	65	6.5	87.9	87.42	84	84.88
4	0	0	0	30	65	6.5	87.8	87.42	82	84.88
5	-1	0	1	25	65	7.5	84	83.92	82	82.52
6	0	1	-1	30	100	5.5	85.5	85.92	90	90.97
7	-1	1	0	25	100	6.5	80	79.74	82	81.5
8	1	0	1	35	65	7.5	77.5	77.67	74	74.47
9	0	-1	1	30	30	7.5	81	80.57	80	79.02
10	1	0	-1	35	65	5.5	85	85.07	86	85.47

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11	-1	0	-1	25	65	5.5	85.4	85.22	86.95	86.52
12	0	-1	-1	30	30	5.5	86.02	85.69	85.7	85.02
13	1	-1	0	35	30	6.5	75.3	75.55	71	72.5
14	0	1	1	30	100	7.5	82	82.33	83.8	81.97
15	-1	-1	0	25	30	6.5	85	85.5	83	84.45
16	1	1	0	35	100	6.5	83.8	83.29	84.8	84.35
17	0	0	0	30	65	6.5	87	87.42	86	84.88

1) Regression Model Equation for COD and Ammoniacal Nitrogen Concentration after Reverse Osmosis

Several external as well as internal parameters and low order interactions are likely to influence a system or process with several variables. To select the statistically significant model for determining the relationship between the response and input (independent variables), investigations on linear, cubic, two factor interaction and quadratic model were done.

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 results, it had been concluded that quadratic model provides an excellent relationship between the response and the independent variables.
From the Table 6 and 7, the coefficient of determination (R^2) of the model was 0.9907(COD) and 0.9362 (Ammoniacal Nitrogen) which indicated a good fit between predicted values and the experimental data points. In addition, this implies that 99.07% and 93.62% of the variations for percent COD and Ammoniacal Nitrogen after reverse osmosis experiment are explained by the independent variables and this also means that model does not explain only about 0.93% and 6.38% 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 and the experimental and predicted COD and Ammoniacal Nitrogen concentrations are shown along with the experimental conditions in Table 4. Based on the model analysis, a quadratic model was chosen to fit the data.

Table 6 Model Summary Statistics for COD Response in Reverse Osmosis experiment

Source	**Std. Dev.**	**R-Squared**	**Adjusted R-Squared**	**Predicted R-Squared**	**PRESS**	
Linear	3.46	0.2790	0.1126	0.2421	268.88	
2FI	3.17	0.5351	0.2562	0.2778	276.61	
Quadratic	0.536	0.9907	0.9788	0.8999	21.67	Suggested
Cubic	0.427	0.9966	0.9865	N/A	N/A	Aliased

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Table 7: Model Summary Statistics for Ammoniacal Nitrogen Response in Reverse Osmosis experiment

Source	Std. Dev.	R-Squared	Adjusted R-Squared	Predicted R-Squared	PRESS	
Linear	3.45	0.5633	0.4625	0.1717	293.82	
2FI	2.96	0.7529	0.6046	0.0870	323.85	
Quadratic	1.80	0.9362	0.8541	0.6578	121.39	Suggested
Cubic	2.04	0.9530	0.8118	N/A	N/A	Aliased

C. 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

For the reverse osmosis experiment, it can be seen that p value for the sequential model sum of squares is less than 0.0001 for COD and greater than 0.0001 for Ammoniacal Nitrogen and F value for COD is (82.94) while that of Ammoniacal Nitrogen is (11.41) 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 0.2137 for COD and 0.7159 for Ammoniacal Nitrogen.

Table 8: Analysis of Variance for COD after Reverse Osmosis experiment

Source	Sum of squares	Degree of freedom	Mean square	F value	P value prob>F	
Model	214.46	9	23.83	82.94	< 0.0001	significant
A	20.48	1	20.48	71.28	< 0.0001	

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Temperature						
B- contact time	1.98	1	1.98	6.89	0.0341	
C- pH	37.93	1	37.93	132.03	< 0.0001	
AB	45.56	1	45.56	158.59	< 0.0001	
AC	9.30	1	9.30	32.38	0.0007	
BC	0.5776	1	0.5776	2.01	0.1992	
A^2	52.32	1	52.32	182.10	< 0.0001	
B^2	34.68	1	34.68	120.72	< 0.0001	
C^2	3.56	1	3.56	12.40	0.0097	
Residual	2.01	7	0.2873			
Lack of fit	1.28	3	0.4277	2.35	0.2137	not significant
Pure Error	0.7280	4	0.1820			
Cor Total	216.47	16				

Table 9: Analysis of Variance for Ammoniacal Nitrogen after Reverse Osmosis experiment

Source	Sum of squares	Degree of freedom	Mean square	F value	P value prob>F	
Model	332.07	9	36.90	11.41	0.0021	significant
A Temperature	41.18	1	41.18	12.73	0.0091	
B- contact time	54.60	1	54.60	16.88	0.0045	
C- pH	104.04	1	104.04	32.16	0.0008	
AB	54.76	1	54.76	16.93	0.0045	

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AC	12.43	1	12.43	3.84	0.0908	
BC	0.0625	1	0.0625	0.0193	0.8934	
A^2	56.36	1	56.36	17.42	0.0042	
B^2	4.39	1	4.39	1.36	0.2821	
C^2	4.35	1	4.35	1.34	0.2843	
Residual	22.64	7	3.23			
Lack of fit	5.96	3	1.99	0.4759	0.7159	not significant
Pure Error	16.69	4	4.17			
Cor Total	354.72	16				

ANOVA table suggest whether the equation is adequate to describe the relationship between response and other independent variables. The model can be considered as statistically significant, if the value of p is lower than 0.05 with a larger F value (Richard et al., 2018). From the Model Summary Statistics table (Tables 10 to 11), it is observed that the quadratic model fitted well with the data generated and can be considered as statistically significant, since the F values are large and p value is lesser than 0.05. In the ANOVA table, AB, A^2, B^2 and C^2 were the significant model terms, whereas other terms are not listed as significant factors since their p values were greater than 0.1. 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 my study, CV obtained for COD and Ammoniacal nitrogen removal by adsorption and reverse osmosis was (1.43%, 0.6140%) and (0.6383%, 2.16%) respectively. Adequate precision value measures signal to noise ratio and a ratio greater than 4 is desirable. The obtained ratio from my research was (23.8229, 24.2966) and (28.8679, 14.2084) for the adsorption and reverse osmosis experiment respectively which indicate an adequate signal.

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

Std Dev.	0.5360	R-Squared	0.9907
Mean	83.98	Adj R- Squared	0.9788
C.V%	0.6383	Pred. R- Squared	0.8999
PRESS	21.67	Adequate precision	28.8679

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

Std Dev.	1.80	R-Squared	0.9362
Mean	83.16	Adj R- Squared	0.8541
C.V%	2.16	Pred. R- Squared	0.6578
PRESS	121.39	Adequate precision	14.2084

D Estimation of Quantitative Effects of the Factors that affects % COD Removal by Reverse Osmosis

From the Figures 2 and 3, it can be deduced that as pH increased from 5.5 to 7, the COD removal percentage also increased from 74% to 83% and this is an indication that the removal of COD by reverse osmosis is more efficient in acidic environment than in alkaline environment. It can also be deduced that the temperature increases from 25ºC to 33ºC led to an increase in COD percentage removal from 75% to 85%. Therefore, it can be concluded that the interaction between temperature and pH as compared to the other interactions has an overall positive effect in the removal of COD from wastewater by reverse osmosis.

From Figure 4, it is observed that as pH increased from 5.5 to 7, the percentage removal of COD by reverse osmosis also increases from 75% to 81% which also conforms to the fact that the COD removal is favored in moderate acidic medium environment. Also, increase in contact time from 30 to 100seconds favors the COD percentage removal as it increases from 75% to 86%. Therefore, it can be concluded that the interaction between contact time and pH has an overall positive effect on the percentage removal of COD by reverse osmosis.

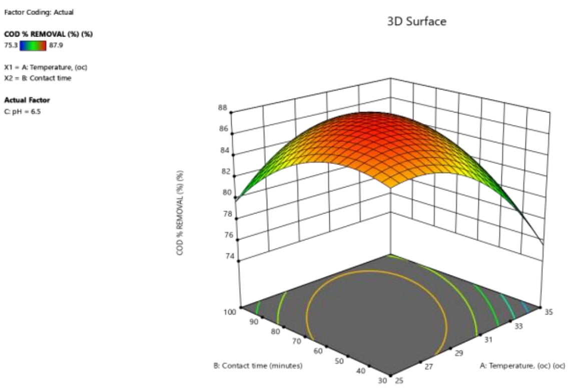

Fig. 2: Surface plot of the predicted COD percentage removal by reverse osmosis as a function of Temperature and contact time with pH fixed at 6.5.

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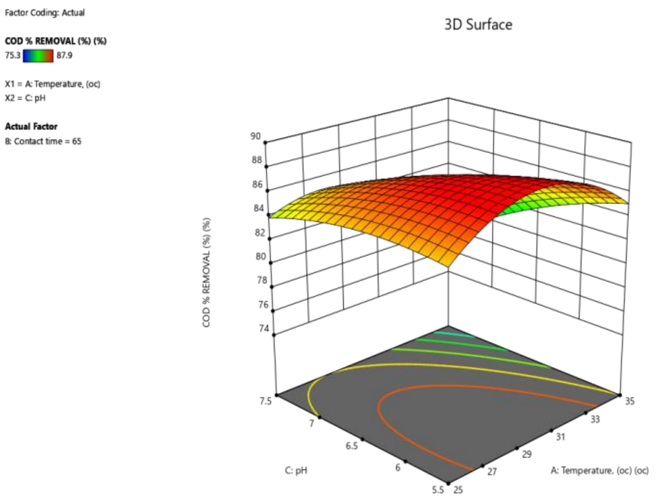

Figure 3: surface plot of the predicted COD percentage removal by reverse osmosis as a function of Temperature and pH with contact time fixed at 65 seconds.

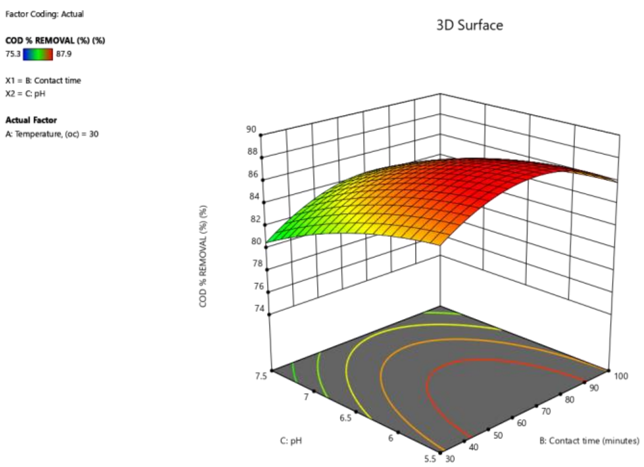

Fig. 4: surface plot of the predicted COD percentage removal by adsorption as a function of contact time and pH with temperature fixed at 30^{o}C.

E. Estimation of Quantitative Effects of The Factors That Affects %Ammoniacal Nitrogen Removal by Reverse Osmosis

From the Fig 5, it was observed that as both contact time increased from 30 to 100seconds, the percentage removal of Ammoniacal Nitrogen also increased from 70% to 81% and this is evident because if the flow of wastewater through the RO membrane is slow, by increasing the contact time, the Ammoniacal nitrogen concentration in the reject increases. The graph also shows that there was an initial increase in Ammoniacal nitrogen removal from 70% to 74% as temperature increases from 25^{o}C to 29^{o}C after which further increase in the temperature led to a drastic decrease in Ammoniacal nitrogen percentage removal to 72%. This can be concluded that the effect of contact time on Ammoniacal nitrogen percentage removal by reverse osmosis overrides that of temperature.

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From the fig 4.15 below, it can be deduced that as pH increased from 5.5 to 7, Ammoniacal Nitrogen percentage removal also increased from 74% to 83%. Also, temperature increase from 25ºC to 33ºC led to increase in Ammoniacal nitrogen percentage removal from 74% to 86% after which further increase in temperature from 33ºC to 35ºC leads to a slight decrease in Ammoniacal nitrogen percentage removal to 84%. Therefore, it can be concluded that the interaction between both factors have an overall positive effect on the percentage removal of Ammoniacal nitrogen from wastewater by reverse osmosis.

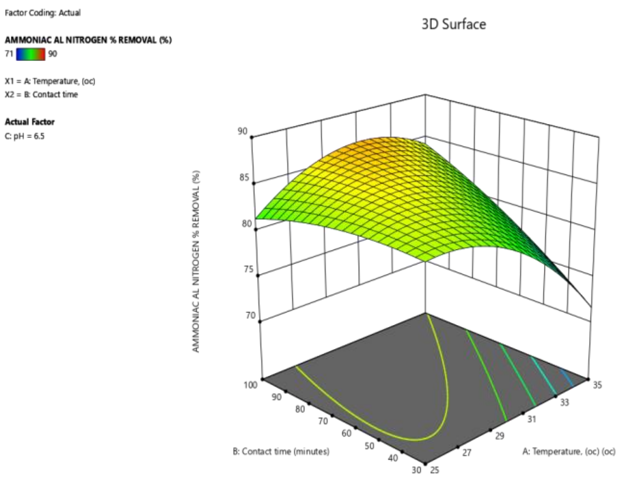

Fig. 5: surface plot of the predicted Ammoniacal Nitrogen percentage removal by reverse osmosis as a function of Temperature and contact time with pH fixed at 6.5.

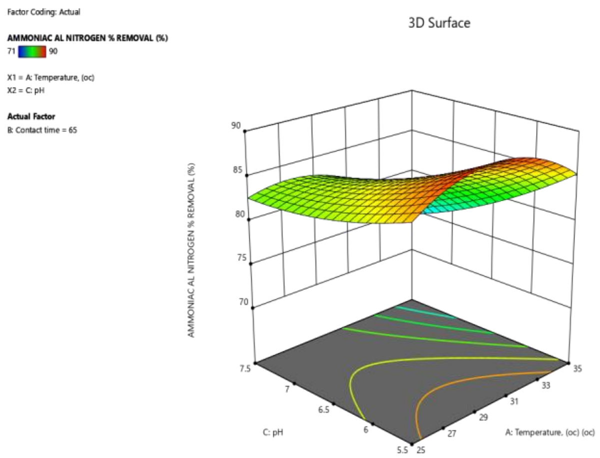

Fig. 6: surface plot of the predicted Ammoniacal Nitrogen percentage removal by reverse osmosis as a function of Temperature and pH with contact time fixed at 65 minutes.

From Figure 7, it is observed that as both contact time and pH increase, percentage removal of Ammoniacal nitrogen also increased. Increase in pH from 5.5 to 7 led to increase in percentage removal of Ammoniacal nitrogen from 68% to 78% while the increase in contact time from 30 to 100seconds led to the increase in percentage removal of Ammoniacal nitrogen from 68% to 91%. Therefore, it can be concluded that the interaction between contact time and pH has an overall positive effect on the percentage removal of Ammoniacal nitrogen from wastewater by reverse osmosis.

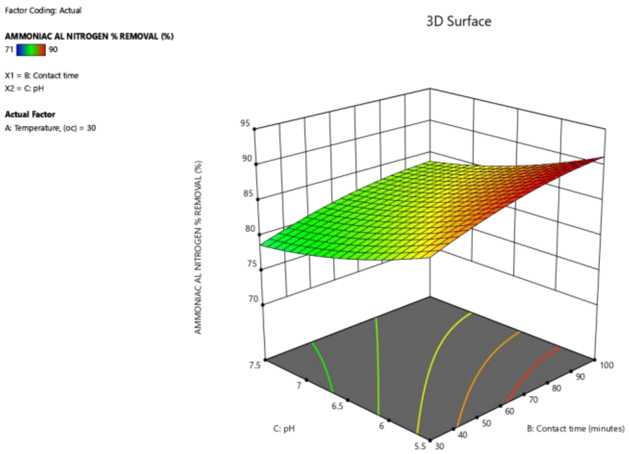

Fig. 7: surface plot of the predicted COD percentage removal by reverse osmosis as a function of contact time and pH with temperature fixed at 30ºC.

IV CONCLUSION

The statistical methodology, Box-behnken response surface methodology was demonstrated to be effective and reliable in finding the optional conditions for the high removal efficiency of COD and Ammoniacal nitrogen by reverse osmosis and the results showed that the parameters considered have significant effects on the COD and Ammoniacal nitrogen removal using reverse osmosis method. The response surface plot was used to estimate the interacting effects of the 3 independent variables (pH, contact time, temperature) on the responses (%COD removal, %Ammoniacal nitrogen removal) and the quadratic model was developed by regression analysis of the experimental data obtained. It could be concluded that the interaction between contact time and pH has an overall positive effect on the percentage removal of Ammoniacal nitrogen as well as COD removal from wastewater by reverse osmosis. Similarly, it could be concluded that the interaction between temperature and pH has an overall positive effect on the percentage removal of Ammoniacal nitrogen from wastewater by reverse osmosis. Optimum temperature for removal of COD by reverse osmosis in this study was 33ºC while optimum temperature for removal of ammoniacal nitrogen was 29ºC; above and below these temperatures there were decline in the contaminants removal. Ammoniacal nitrogen removal with reverse osmosis was about 91% maximum. As pH increased to 7.0 from 5.5 there was increase in ammoniacal nitrogen removal from 68% to 78% the percentage removal of COD by reverse osmosis also increases from 75% to 81% which also conforms to the fact that the COD removal is favored in moderate acidic medium environment. Also, the increase in contact time from 30 to 100seconds led to the increase in percentage removal of Ammoniacal nitrogen from 68% to 91% and favors the COD percentage removal as it increases from 75% to 86%.

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