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Optimization of the Removal of Antibiotics from Pharmaceutical Wastewater on Activated Carbon Using Response Surface Methodology

Salisu Sani[1], Adamu Musa Mohammed[2], Abdulrahman A. Abdulrasheed[3]

[1,2,3] Department of Chemical Engineering, Abubakar Tafawa Balewa University Bauchi, Bauchi State – Nigeria

ABSTRACT: The improper disposal of antibiotics by pharmaceutical industries poses significant risks to both human health and the ecosystem. Although the concentration of these antibiotics in pharmaceutical wastewater may appear insignificant, studies have revealed that these substances are non-biodegradable and contribute to the emergence of antibiotic-resistant bacteria known as superbugs. This research aims to optimize the removal of antibiotics from pharmaceutical wastewater using activated carbon and response surface methodology (RSM). The study investigates the impact of experimental variables, namely adsorbent dose, contact time, and pH, on the removal of ampicillin. The proximate analysis of the produced adsorbent reveals ash content, moisture content, and pH values of 6.79%, 13.27%, and 8.73, respectively. The FTIR analysis confirms the presence of the –OH– functional group resulting from the activation process with KOH, which enhances the adsorption process. The study identifies the optimal conditions for ampicillin removal as follows: a contact time of 26.3 minutes, an adsorbent dose of 341.4 mg, and a pH of 7.6. Under these conditions, the removal efficiency reaches 84.36%. The analysis of variance demonstrates that the developed model effectively represents the experimental data, and validation results indicate a margin of error of approximately 2.7%, which falls within an acceptable range. Consequently, this research concludes that the implementation of Central Composite Design (CCD) based on RSM successfully optimizes the removal efficiency of ampicillin from pharmaceutical wastewater.

KEYWORDS: Antibiotics, Improper disposal, Superbugs, Proximate Analysis, and Adsorption.

I. INTRODUCTION

Improper disposal of antibiotics has become a great concern to researchers worldwide[1], [2]. Antibiotics are of great importance as they are used in the treatment of infections related to both humans and animals[3]. The major sources of antibiotics in the aqueous environment mainly originate from pharmaceutical industries, hospital effluents, and municipal wastewater [4]. Although the concentration of antibiotic residues in the environment is low studies have revealed that these antibiotics are practically non-biodegradable and may result in the production of antibiotic-resistant bacteria and antibiotic resistance genes (ARGs)[2]. Among the various pharmaceuticals, antibiotic usage has rapidly increased all over the world, thus it has received widespread attention [5]. Residual antibiotics in the water environment increase the resistance of pathogenic bacteria and pose a great threat to groundwater and surface water; therefore, it remains a challenge to remove antibiotics from aqueous solutions[6].

Ampicillin is a β -lactam, “broad spectrum” penicillin group antimicrobial agent which is used in treatments against Gram-positive and Gram-negative bacteria. Several methods have been developed to deal with antibiotic contaminations in wastewater, including oxidation, reverse osmosis, coagulation, nanofiltration membranes, photocatalytic degradation[7]–[14], and adsorption[2]. Although processes such as advanced oxidation can convert antibiotic molecules into simple compounds or even mineralize them completely these processes are very expensive and difficult to maintain for the total removal of compounds including antibiotics at an industrial scale. Thus, physicochemical technologies are proving to be highly suitable treatment options for organic contaminants. The adsorption process is very efficient, simple to design and operate; and it is relatively inexpensive and unaffected by the potential toxicity for biologically based processes [5], [15]. Among the current methods for removing antibiotics from pharmaceutical industries, hospital effluents, and municipal wastewater, adsorption is considered to be an excellent method for the treatment of wastewater containing low concentrations of antibiotics because of its high efficiency and antitoxic nature [6], [16].

The choice of adsorbent is the most critical factor in adsorption[17]. Carbon adsorbents are widely used because they have the advantages of acid and alkali resistance, strong adsorption capacity, and stable properties[18]. Considerably, researchers have focused on adding chemical modifying agents for improving the adsorption capacities of carbon adsorbents, pore structure, and abundant surface function group, thus having an excellent adsorption removal capacity for antibiotics(i.e. surface chemistry) [6].

Activated carbons have a wide range of properties and physical forms making them to be prominently used in many applications. They are extensively used in a variety of industrial and environmental applications. The important properties such as surface area, pore volume, and pore size distribution are among those that are strongly associated with the adsorption capacity. Pore size distribution with the combinations of the micropores (pore diameter < 2nm) and mesopores (pore diameter 2 – 50 nm) are required to improve the transport process of particles or molecules inside porous networks and facilitate the adsorption of molecules [19]. Due to their excellent characteristics, activated carbons have increasingly been used in numerous practical applications. Consequently, the world consumption of activated carbon has steadily increased and also not been replaced until now, despite hard competition from zeolites, polymers, and other new adsorbents [19], [20] .

II. EXPERIMENTAL

A. Material and Methods

Ampicillin Sodium was procured from Anhui Chengshi Pharm. Co. Ltd with NF REG A4-6912, and the Reagents (Hydrochloric acid, Potassium Hydroxide, and Sulfuric acid) were obtained from NAZOP laboratory, Chemical Engineering department Abubakar Tafawa Balewa University, Bauchi.

The equipment and apparatus used were; Analytical Balance (LA164; B. Bran Scientific), Sieve 0.18mm-300nm, Muffle Furnace (NCPRD/ECN/ATBU/LAB/EFN/197 NYC-12), pH meter, Conical Flasks, Beakers (Erlen-meyer), Oven, Orbital Shaker (Coslab ISO 9001 co), Volumetric Flasks, Whatman Filter Paper, UV-Vis Spectrophotometer (752N).

B. Chemical Activation of Adsorbent

The activated carbon (adsorbent) was chemically prepared with Potassium Hydroxide (KOH) at a 2:1 ratio to achieve the desired formation of micropores and was heated to 600ºC for 1 hour. The activated adsorbent was then sieved to 0.18mm - 300µm for proper size distribution and washed with 1M solution of HCl acid and then with distilled water until the pH was 7[17], [21]. The activated adsorbent was then oven-dried overnight at 85ºC and stored[22].

C. Experimental Design and Procedure

The experiment was designed using Central Composite Design (CCD) under Response Surface Methodology (RSM) to optimize the experimental variables which include pH, adsorbent dose, and contact time with a total of 20 runs as shown in TABLE I and the entire design matrix was developed using Design Expert V 11.1.2.0. The maximum and minimum levels used for the factors considered were shown in TABLE I.

Equation of the Calibration Curve, Fig 1 was determined by varying the concentrations of ampicillin in simulated pharmaceutical wastewater from 0.5 mg/ml – 2 mg/ml at 0.25 mg/ml concentration increment and the concentration was spectrophotometrically determined at 511 nm wavelength[2], the absorbance obtained was plotted against concentration.

TABLE I: Minimum and maximum levels of the experimental factors

S/N	Variable	Unit	Minimum	Maximum
A	Adsorbent Dose	Mg	250	500
B	Contact Time	Min	15	45
C	pH	-	5	9

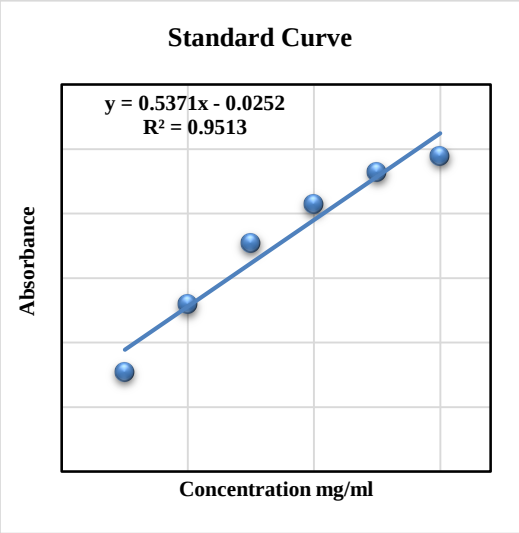

Figure 1: Derivation of Standard Curve Equation

The experiment was conducted according to the Design of Experiment (DOE), 50 ml samples tagged 1 – 20 with different pH, and adsorbent doses, were placed on a rotary shaker Fig 2 and 3 in a 100 ml beaker at 180rpm and each sample was removed at predetermined contact time where it was filtered, and its absorbance was measured spectrophotometrically using UV Vis Spectrophotometer.

Using the standard curve, the resulting concentration and percentage adsorbed were calculated using equation 1.

Figure 2: Samples on Rotary Shaker

Figure 3: Pharmaceutical Wastewater in sample bottles

$$\text{Removal (\%)} = \frac{(Ci - Cii)}{Ci} \times 100 \quad (1)$$

Where Ci is the initial concentration of the stock solution which was 1.5 mg/ml, Cii is the concentration after adsorption.

D. Central Composite Experimental Design

CCD gives almost as much information as a three-level factorial, requires many fewer tests than the full factorial design, and is sufficient to describe the majority of steady-state process responses. Hence in this study, it was decided to use CCD to design the experiments. The number of tests required for CCD includes the standard 2k factorial with its origin at the center, 2k points fixed axially at a distance, say β, from the center to generate the quadratic terms and replicate tests at the center, where k is the number of variables. The axial points are chosen such that they allow rotatability, which ensures that the variance of the model prediction is constant at all points equidistant from the design center[23].

In most cases, the RSM follows second order polynomial model as

$$Y = \beta_{\circ} + \sum_{i=1}^{k} \beta Xi + \sum_{i=1}^{k} \beta Xi^2 + \sum_{i=1}^{k-1} \sum_{j=i+1}^{k} \beta ijXij. \quad (2)$$

Where Y is the predicted response: *X1, X2,…Xk* are input factors that influence the response *Y;* $\beta_{\circ}$ is a constant, βi is a linear term coefficient, βii is a quadratic term coefficient and βij is cross product term coefficient and k is the number of factors.

TABLE II: Experimental Design

	Independent Variables			Percentage Removal	
Run	**A: Adsorbent Dose (mg)**	**B: Contact Time (min)**	**pH**	**Actual Removal %**	**Predicted Removal %**
1	375	30	10	78.45	80.68
2	375	30	7	84.34	84.16
3	165	30	7	81.20	82.20
4	250	15	9	82.60	81.65
5	375	30	7	84.30	84.16
6	500	15	9	81.30	79.67
7	375	5	7	74.20	75.20
8	250	45	9	83.24	81.61
9	500	45	5	78.00	78.24
10	375	30	4	81.32	80.09
11	500	45	9	70.12	70.01
12	250	45	5	77.43	78.35
13	250	15	5	73.32	72.72
14	375	30	7	84.06	84.16
15	375	30	7	84.12	84.16
16	500	15	5	81.31	82.23
17	375	30	7	84.21	84.16
18	375	30	7	84.12	84.16

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A. Characterization

The physicochemical characteristics of the Palm Shell Char used in this study are summarized in TABLE III. Ash content and moisture content recorded on a dry basis were 6.79% and 13.27% respectively and pH was 8.73. The spectra of activated carbon were measured within 4000 – 500/cm wave number. Figure 4 is the FTI-R spectra of an unwashed activated carbon before adsorption, the peaks at 1994.1 is identified as -OH- stretching which was due to the activation with KOH which enhances the adsorption process, while peaks 2111.5 cm-1 and 2089.2 cm-1 are identified as N-H vibration with medium absorption intensity with 1500 cm-1 as the fingerprint region. As seen in Figure 4 the peaks recorded proves that the sample was washed with an acid that neutralize the presence of some of the functional groups whereas some of the functional group were grafted to the surface of the adsorbent as seen in Fig 12 [20], [24], [25].

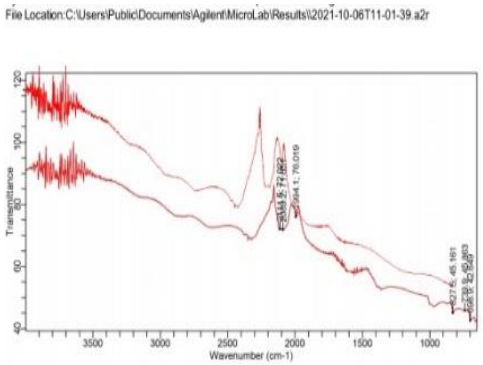

Figure 4: Spectra of Palm Shell Activated Carbon

TABLE III: Result of Proximate Analysis

Sample	Ash%	Moisture %	pH
PMS AC 1	7.3	12.9	8.7
PMS AC 2	6.75	13.4	8.67
PMS AC 3	6.32	13.51	8.82
AVERAGE	6.79	13.27	8.73

TABLE IV: Fit Summary

Source	Sequential p-value	Lack of Fit P-value	Adjusted R^2	Predicted R^2
Quadratic	0.0002	< 0.0001	0.8859	0.1508

In Table IV the RSM generated a series of models which were Linear, Two Factor interaction (2FI), Quadratic, and Polynomials that fitted the response as well as suggested the best model that fits the data as shown in TABLE V. According to the sequential model sum of squares, the best model that best fits the response was the quadratic model due to its highest order of polynomial with the significance of additional terms, but the cubic model was aliased. The quadratic model was selected because it has the highest R2 (0.8859) value compared to other models.

TABLE V: Final Equation in Terms of Actual Factors

Percentage Removal	
-7.81985	
+0.162856	Adsorbent Dose
+1.74885	Contact Time
+10.48537	pH
-0.001283	Adsorbent Dose * Contact Time
-0.011490	Adsorbent Dose * pH
-0.047250	Contact Time * pH
-0.000064	Adsorbent Dose^2
-0.016736	Contact Time^2
-0.333731	pH^2

Table V shows the relationship between the dependent variable (%Removal) and the independent variables (Contact Time, Adsorbent dose, and pH), which is the model equation obtained through regression analysis that represents the removal efficiency where the positive and negative signs imply synergism and antagonistic effect between the independent variables.

B. ANOVA for Quadratic Model

TABLE VI presents the Analysis of Variance (ANOVA) in which the model and the lack of fit were significant, the A2 (Adsorbent) under the P-value which is greater than 0.05 is not significant whilst the other factors that affect adsorption has a P-value below 0.05. This implies that an increment in the dosage has no significance on the adsorption efficiency. The F value indicates that most of the variation in the response can be explained by the regression equation. The P-value is used to estimate whether F is large enough to indicate statistical significance.

TABLE VI: Analysis of Variance for Quadratic Model

	Sum of Squares	Df	Mean Square	F-value	p-value	
Model	298.1	9	33.12	15.66	0.000	significant
A	2.37	1	0.37	1.12	20.320	
B	8.84	1	8.84	4.18	0.075	
C	0.412	1	0.412	0.195	0.671	
Lack of Fit	16.86	3	5.62	455.43	< 0.0001	significant

C. Interaction Between Adsorption Factors

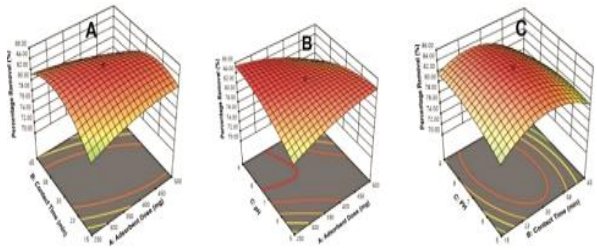

Figure 5: Response surface plot combining (A) Adsorbent Dose (mg)/Contact Time (min) against %Removal (B) Adsorbent Dose(mg)/pH against %Removal and (C) Contact Time(min)/pH against %Removal.

It could be seen from Figure 5, 3-D surface plots that A which is the removal efficiency to residence time Adsorbent dosage increases and then start to decrease as the time increases in which the optimum residence time was seen to be approximately 30 mins. From B it could be seen that the relationship between adsorbent dose and removal efficiency was close to linear as such the more the dosage the more the percentage removal and the pH was optimum towards the basic region, and this was due to the nature of the adsorbate which is a weak conjugate acid. In C a relationship similar to the one in A is maintained

D. Optimization and Model Validation

The predicted optimum condition for maximum removal of ampicillin from pharmaceutical effluents using palm shell activated carbon has been predicted using the Design Expert's

optimization option in terms of upper and lower limits for the selected variables which were contact time, adsorbent dose, and pH. The conditions with their predicted value values were 341.4 mg, 26.3 min, 7.6 and adsorbent dose, contact time, and pH respectively with a removal efficiency of 84.4%. To further verify the result obtained from statistical analysis of CCD a verification experiment was conducted under the same optimum condition obtained from RSM and the verification experiment was validated with a margin error of 2.7%.

CONCLUSIONS

In this study, the application of activated carbon to the removal of antibiotics from pharmaceutical effluent was investigated using RSM by varying the independent variables (contact time, adsorbent dose, and pH). The effect of these variables on the removal efficiency was vividly explained by the result obtained from RSM and was used to optimize the maximum percentage removal. It was shown that the regression model that best fits the result was the second-order polynomial equation and the coefficient of determination (R2) was found to be 88.6%. The result also shows that the optimum condition for the removal of antibiotics from pharmaceutical effluent was 341.4 mg, 26.27 min, and 7.6 adsorbent doses, contact time, and pH respectively with a maximum removal efficiency of 84.36%. The predicted result was validated and an error of 2.7% was obtained which indicates that the model was significant since the error was less than 5%. The RSM and CCD optimization tools are effective in determining the optimum condition for the process and the interconnected relationship among process parameters.

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