

(Research Article)

Experimental Design for Optimal Removal of PAH from Crude Oil Waste using Aerobic Bioreactor

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Abstract

Crude oil waste contains recalcitrant pollutants and bioreactors offer a significant mechanism for the removal of these pollutants. The present work is concerned with the finding of the optimum conditions for removal of polycyclic aromatic hydrocarbons (PAHs) using bioreactors from crude oil sludge. The Box-Wilson method of experimental design was adopted to establish relationships between three operating variables (dosage of oxygen, PAHs concentration and pH) that affect the treatment process. The experimental data were successfully fitted to a second-order polynomial mathematical model which was used to optimize the treatment process in discontinuous mode at laboratory scale. The most favorable operating condition for the treatment include; oxygen dosage (0.4g), PAHs concentration (20mg/L) and pH (6). On using the optimum conditions, a mathematical model simulating the treatment process was obtained. The results show that the bioreactor is very effective in removing PAH from crude oil sludge.

Keywords: PAH, Bioreactors, Experimental design, Optimization.

1. Introduction

The oil industry generates large quantities of oily and viscous residues, which are formed during production, transportation and refining [1]. These residues, called oily sludges, are composed of oil, water and solids [2]. This constitutes a multiphase system; making the residues highly recalcitrant and very difficult to reutilize. The marked stability of this multiphase system is due to the adsorption of oil into solid particles, producing a highly protective layer (as they tend to settle to the bottom of the tanks), and also due to the presence of surface-active compounds, which are responsible for the formation of emulsions. Additionally, the presence of organic polar fractions brings about charge repulsion, impairing the formation of a homogeneous phase [3]. From a chemical point of view, recalcitrance can be ascribed to the presence of aromatic hydrocarbons, polycyclic aromatic hydrocarbons (PAHs) and complex compounds with a very high molecular weight, such as asphaltenes [4].

It is estimated that approximately 1% of the total oil processed in Port Harcourt Refinery, Nigeria, is discharged as oily sludge, usually after being accumulated in storage tanks

for several years [5]. Incineration of this sludge is not recommended due to the high energy costs involved, the potential risk of air pollution and the persistence of PAHs. Similarly, the inadequate disposal of such a very toxic residue in landfills encourages the search for alternatives

The use of biological processes to treat waste or waste contaminated material is well-documented [6]. Bioprocess involves exploiting abilities of indigenous dosage or augmented microorganisms to metabolize organic substrates [7]. It can be accomplished in a land-based environment (landfarming, composting or biopiling) or in some cases bioremediation may be carried out in-situ by enhancing microbial degradation of contaminants in the subsurface of soil. In other cases, contaminated material may be treated in slurry bioreactors to degrade petroleum hydrocarbons. The process of landfarming has been implemented worldwide as a means of biological treatment and disposal of oily sludges [7]. The sludges are sprayed on land together with fertilizers and the soil is tilled to promote the activity of natural soil microbial population for the degradation of petroleum hydrocarbons. Although landfarming may be a low cost method if land is available, it requires very long treatment times due to lack of control on environmental factors such as seasonal variation in temperature, pH, moisture, natural

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microbial activity, mixing and circulation limitations [8]. In climates with limited rainfall, the cost to maintain the proper moisture content in the soil could be prohibitive. Lack of uniformity causes high contaminant concentration/toxicity in localized pockets and inconsistent permeability of soil makes it difficult to apply treatment additives like nutrients and oxygen [9]. Care also needs to be taken to ensure that landfills are isolated from watercourses. Most of the above limiting factors are eliminated in employing bioreactor technology. It eliminates the need to spray high concentrations of petroleum hydrocarbons on large areas of land.

Bioreactors allow the control of optimum process conditions required in the waste treatment. This allows for a higher quality final effluent in a shorter period of time, although costs are significantly higher. Despite their potential, the use of bioreactors is limited and most studies have focused on synthetic residues ([2]; [1]). However, promising results have been obtained for the treatment of an oily industrial sludge in a stirred bioreactor [10]. Similarly, Valero Refining Company has, for the first time, developed a process using a bioreactor on an industrial scale that was both economically viable and environmentally friendly [11].

This study is therefore focused on assessing the effects of various operational parameters, including pH, PAH and oxygen concentration on the rate of the bioremediation of oily sludge using design of experiments (DOE) and to optimize the treatment processes in a laboratory scale mechanically stirred-tank bioreactors. The statistical models were validated by an additional set of experiments at the optimum conditions in line with the DOE results.

2. Materials and Methods

2.1. The Reactor/Major Apparatus

The experimental investigations were conducted in the elaborate laboratory bioreactor 2L-M with disk magnetic coupling as well as sliding bearings and maximum volume 2L. The bioreactor was included in an automatic control system (ACS). ACS was developed as three different blocks: in block dosimeters: the dosimeters for passing base, acid and foam slacked; and in block transformers- transformers for the basic measured values. The system, under control of a computer, allowed for regulation of parameters of the treatment process: pH, PAH concentration and oxygen dosage.

2.2. Mode of Data Collection

The oily sludge was sampled from the Port Harcourt refinery in Rivers state, Nigeria. In order to achieve pH and alkalinity adjustment, the supernatant was neutralized with NaOH and NaHCO₃. The ratio of COD: N: P was 300:5: 1 and this was kept during operation using NH₄Cl and

K₂HPO₄. The micro-nutrient deficiency was added occasionally to correct growth conditions according to [12]. The initial oil and grease, paraffins and polyaromatics content of samples were determined before the experiment. Duplicate samples were withdrawn from the bioreactor and the organic phase is extracted by n-hexane in a separation funnel, passed through a layer of Na₂SO₄ in order to remove the humidity. Finally, the hydrocarbon consumption was evaluated by determining the oil and grease [13], paraffins (nC₁₀ to nC₃₄, pristane, phytane) by Gas Chromatography using a flame ionization detector, and total polyaromatics by UV absorption in the wavelength range of 220 - 450 nm [11]. The Taguchi & Humphrey method [14] was adopted to evaluate the Oxygen Uptake Rate (OUR) required by interrupting aeration and monitoring the decrease of oxygen concentration in the bioreactor. Specific Oxygen Uptake Rate (SOUR) was expressed as a function of the microbial biomass as measured by plate counts, assuming 10¹² cells g⁻¹ bacteria and 10⁹ cells g⁻¹ yeast [15].

The sludge was fed to the reactor with the help of a variable speed peristaltic pump. The reactor was operated at various hydraulic retention times (HRTs) by varying the flow rate of influent wastewater (Q_{inf}), thereby varying the loading rate (LR). At any given loading rate, the bioreactor was continuously operated until steady-state condition was achieved, when gas production rate in bioreactor became constant. Then effluent samples were collected and subjected to the analysis of the following parameters, i.e. influent and effluent COD, oil and grease, paraffins and total polyaromatics. Experiments were carried out as functions of oxygen dosage, PAH concentration, and pH. To determine the effect of experimental factors on the bioreactor process, this method was also applied at different oxygen dosage, PAH concentration, and pH of the sludge suspension

2.2. Experimental Design and Optimization

A three-factor along with three levels (high, middle and low) in conjunction with response surface methodology (RSM) was used to maximize PAH removal. pH (X₁), initial PAH concentration (X₂) and oxygen dosage (X₃) were used as independent factors in the DOE; whereas, the PAH removal (Y) was considered response variable. Thus, each factor was coded at three levels, from -1 to +1, as shown in Table 1. A previous study [16] was used to determine and select the critical ranges of the factors. The model responses were formulated as a quadratic model shown as Equation (1) and estimate of the model parameters represented by coefficients of Equation (1) were evaluated by least-squares regression according to Montgomery [17].

$$y = \beta_0 + \sum_{i=1}^k \beta_i X_i + \sum_{i=1}^k \beta_{ii} X_i^2 + \sum_{i=1}^{k-1} \sum_{j=2}^k \beta_{ij} X_i X_j + C \quad (1)$$

where β_0 , β_i , β_{ii} , and β_{ij} are the constant, linear, quadratic, and cross-factor interaction coefficients, respectively; X_i and

X_j represent the coded independent variable and i or j is the number of independent variables; Y_i is the predicted response; and c and k are the residual term and the number of factors, respectively.

Table 1: Coded levels of Factors for 3^3 Central Composite Design (CCD)

Factors	Levels of Factor		
	Low (-1)	Middle (0)	High (+1)
pH (X_1)	4	7	10
Concentration (mg/L) (X_2)	50	100	150
Adsorbent dosage (g/L) (X_3)	0.5	1	1.5

The Design-Expert 9.0.4.1 statistical software was employed for graphical and regression analysis to estimate the coefficients of the response functions. The significance of the independent variables, factor interactions, and model equations were examined by analysis of variance (ANOVA) at 95% confidence intervals (CI). Three-dimensional (3D) surfaces and two-dimensional (2D) contour plots were obtained while keeping another factor constant in the quadratic models. Additional experiments were carried out to validate the statistical models for maximum PAH removal. Optimal operating conditions were estimated using the numerical optimization method built in the software. Lastly, an additional experimental run was carried out to validate the predicted optimal conditions for the response function for the removal of PAH. The desirability multiple response method was used to combine the desirable ranges for the response to obtain a simultaneous objective function that represents the geometric mean of all transformed responses as given by Myers [18] in Equation (2).

$$D = (d_1 \times d_2 \times \dots \times d_n)^{\frac{1}{n}} = \left(\prod_{i=1}^n d_i \right)^{\frac{1}{n}} \quad (2)$$

where D , d_i , and n are the desirability objective function, response range, and the number of responses, respectively. If the analyzed response is found to be outside of the desirability range, the overall desirability function becomes zero. Therefore, for a simultaneous optimization, response is required to be assigned low value for optimization. In this case, the percent removal of PAH (d_1) was maximized.

3. Results and Discussion

Table 2 shows the three-factor, three-level CCD with observed and predicted values for PAH removal by the developed quadratic models. Thus, to predict the response function for PAH removal, the second-order polynomial Equation (3) was developed:

$$Q = 78.72 + 11.33X_1 + 17.15X_2 - 13.78X_3 + 7.05X_1X_2 - 10.26X_1X_3 + 9.96X_2X_3 - 3.27X_1^2 - 8.86X_2^2 - 1.69X_3^2 \quad (3)$$

Equation (3) shows that among the factors considered in the experiment, the initial PAH concentration was the most influence on the amount of PAH removed. However, the model showed that to obtain good removal of the PAH, pH (X_1) must be increased. The model also showed that the first-order interaction between pH and the oxygen dosage (X_1X_3) and the dual interaction of initial PAH concentration (X_{22}) were also important. In the model, certain factors such as the coefficient associated with the dual interaction of pH (X_{12}) and oxygen dosage (X_{32}) had very low values and a test of significance model coefficients was used to verify that these terms were not influential.

Negative coefficients for the model components X_3 , X_1X_3 , X_{22} , indicate unfavorable effects on the PAH removal. Whereas, positive coefficients for X_1 , X_2 , X_1X_2 , X_2X_3 , indicate favorable effects on the PAH removal. The model showed that when the PAH concentration (X_2) and pH (X_1) were increased, the amount removed (Y) increased. The oxygen dosage (X_3) had a negative effect on the PAH removal (Y).

However, the positive effect on the amount of PAH removed (Y) by the interaction effects between PAH concentration and the oxygen dosage (X_2X_3) implied that the oxygen dosage (X_3) have much less effect on the amount adsorbed (Y) than the PAH concentration (X_2) under high concentration conditions. This is shown in Figure 1(a). As shown in Figure 1b, the effect of negative interaction between the pH and the oxygen dosage (X_1X_3) means that pH had much more positive effects on the amount of PAH removed (Y) than the oxygen dosage X_3 .

Likewise, double interaction effects of PAH concentration (X_{22}), pH (X_{12}) and oxygen dosage (X_{32}) have negative effects on the amount removed such that a decrease in any of these factors causes a decrease in the amount removed.

3.1. Analysis of Variance (ANOVA)

The ANOVA results for the coded quadratic model for the response are reported in Table 3. In terms of coded factors, the models can be described by the following Equation (4), after discarding the insignificant terms:

$$Q = 78.72 + 11.33 X_1 + 17.15 X_2 + 13.78 X_3 + 7.05 X_1 X_2 - 10.26 X_1 X_3 + 9.96 X_2 X_3 - 8.86 X_2^2 \quad (4)$$

Table 2: 3³ Factorial CCD with Observed and Predicted PAH removal (Y)

Run	Coded values			Experimental value			response Y (mg/g)
	X1	X2	X3	X1	X2	X3	
1	-1	0	1	4	100	1.5	54.95
2	0	0	0	7	100	1	80.24
3	1	0	1	10	100	1.5	64.3
4	-1	1	0	4	150	1	72.47
5	0	1	1	7	150	1.5	78.29
6	1	0	-1	10	100	0.5	113.07
7	0	-1	1	7	50	1.5	31.15
8	0	0	0	7	100	1	81.33
9	0	0	0	7	100	1	77.11
10	0	0	0	7	100	1	75.75
11	1	-1	0	10	50	1	46.59
12	-1	-1	0	4	50	1	45.23
13	0	0	0	7	100	1	79.15
14	1	1	0	10	150	1	102.04
15	-1	0	-1	4	100	0.5	62.67
16	0	-1	-1	7	50	0.5	77.93
17	0	1	-1	7	150	0.5	85.28

Fisher's (F) exact test and comparing probability (p) values greater than F. The "Prob >F" less than 0.05 indicated that model was significant. Especially larger F-value with the associated P value (smaller than 0.05, confidence intervals)

means that the experimental systems can be modelled effectively with less error ([19], [20], [21]). Consequently, the model F-value for PAH removal implied that the model was significant. The results of the analysis of variance are summarized in Table 3. Table 3 shows that the interaction effects between the pH of the oily sludge and the PAH concentration (X1X2), between the pH and the oxygen dosage (X1X3), between the PAH concentration and the oxygen dosage (X2X3) and the dual interaction of the PAH concentration (X22) were statistically significant in the AO7 dye removal, with p-values of 0.0417, 0.0085, 0.0099 and 0.0149, respectively. As against the dual interaction effects of pH (X12) and dual interaction of the oxygen dosage (X32) which were not statistically significant on the removal of PAH with p-values of 0.5590 and 0.2745, respectively.

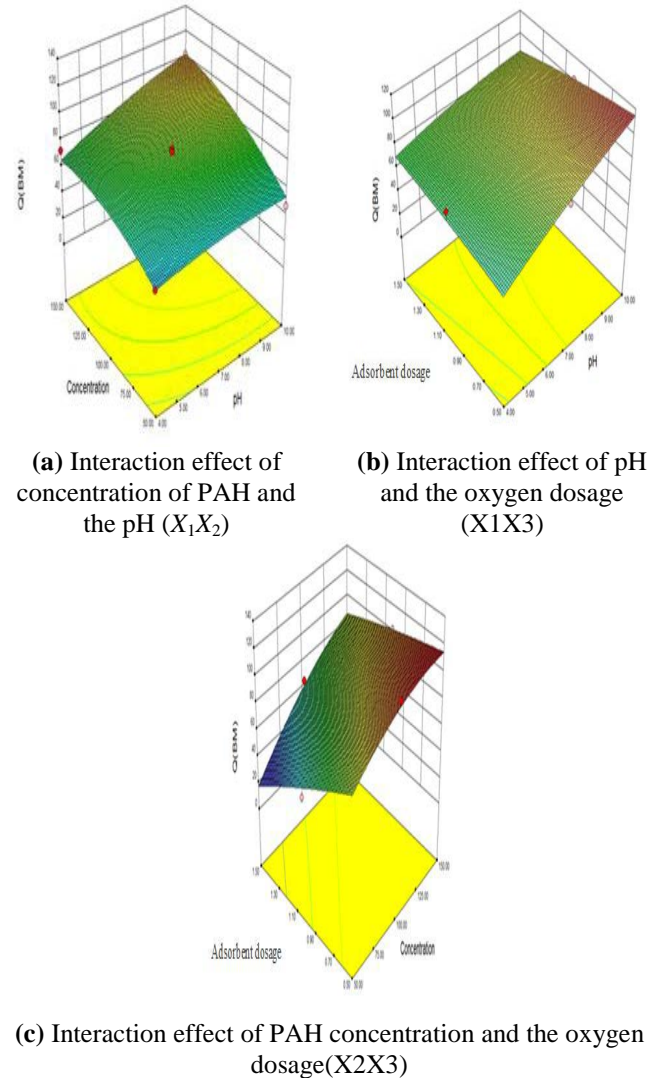


Figure 1: Surface Plots of Cross Factor Interaction

3.2. Model Diagnosis

The goodness of fit of the developed models was validated by the determination coefficient (R²) and the adjusted R² that ensure an adequate variation of the quadratic model to the

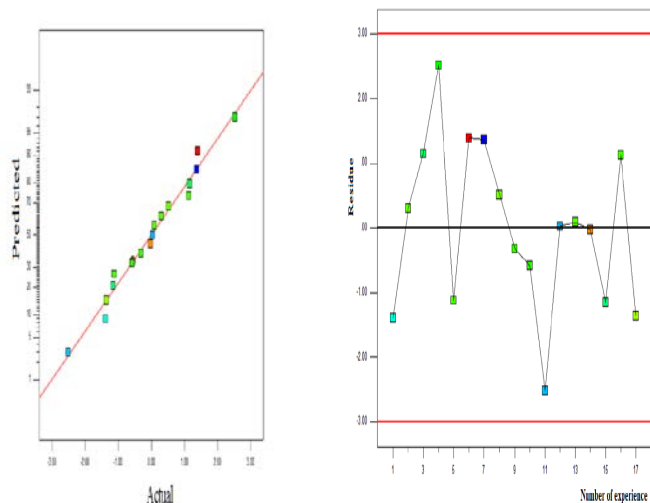
Table 3: ANOVA for Predicted Results for PAH removal (Y)

Source	Sum of squares	Df	Mean square	F value	p-value Prob > F
Model	6329.148	9	703.239	21.891	0.0003
X ₁ -pH	1027.858	1	1027.858	31.996	0.0008
X ₂ - Concentration	2352.294	1	2352.294	73.223	<0.0001
X ₃ - absorbent dosage	1519.658	1	1519.658	47.305	0.0002
X ₁ X ₂	198.951	1	198.951	6.193	0.0417
X ₁ X ₃	421.276	1	421.276	12.117	0.0085
X ₂ X ₃	395.811	1	395.811	12.321	0.0099
X ₁ ²	45.140	1	45.140	1.405	0.2745
X ₂ ²	330.469	1	330.469	10.288	0.0149
X ₃ ²	12.086	1	12.086	0.376	0.5590
Residual	224.874	7	32.125		

experimental values. The values of R² and adjusted R² were found to be 0.9963 and 0.9928 for the PAH removal representing an adequate model's significance. The correlation between the observed and predicted values is shown in Figure 2(a) for PAH removal. As a result, minor discrepancies are represented by a straight line trend, which indicates a good agreement between observed and predicted values. Hence, the quadratic model for the prediction of PAH removal is satisfactory. These values for the model are close indicating a correspondence between the mathematical model and the experimental data. Figure 2(b) shows the residual values. It shows that the residue does not exceed the amount adsorbed, which is of the order of magnitude of the variety of experimental results due to handling. This residue is evenly distributed in space.

3.3. Optimization of Operating Conditions

The RSM was used to calculate the optimum conditions for



(a) Experimental and predicted response for AO7 dye removal

(b) Analysis of Residual for the Response

Figure 2: Tests of Model Assumptions

the three independent variables to get maximum percent PAH removal. Equation (4) was defined as objective functions for PAH removal, and the independent factors in their range were used as model constraints. Thus, the following optimum conditions to reach a maximum PAH removal of 98.9% were found: dosage of oxygen (0.4g), initial PAH concentration (20mg/L) and pH (6). The obtained optimal operating conditions were used in an additional run to validate the predicted values. A PAH removal of 97.8% was obtained experimentally, confirming the reliability of the model since the values are within the 95% CI.

4. Conclusions

In this study, experimental design was used to optimize the PAH removal from crude oil sludge using laboratory scale mechanically stirred-tank bioreactor and determine the effects of the operational factors (pH, initial PAH concentration and oxygen dosage) on the removal of PAH. The interaction effects of pH, PAH concentration and oxygen dosage had a significant effect on PAH removal. To achieve maximum PAH removal, optimum conditions were found for each variable as dosage of oxygen (0.4g), initial PAH concentration (20mg/L) and pH (6). The results obtained in this study show that the laboratory scale mechanically stirred-tank bioreactor is effective for the removal of PAHs from crude oil sludge. The developed mathematical model provides a comprehensive exploration of the cross-factor interactive effects of the independent variables on the responses. Future investigations should be conducted with a view to selectively separating other oily sludge contaminants, regenerating the exhausted biomass, recovering the removed PAH and designing to continuous oily sludge treatment systems. The result of the study produced a model that

estimates the effect of pH, initial PAH and oxygen concentration on the rate of the bioremediation of oily sludge and optimized the treatment processes in a laboratory scale mechanically stirred-tank bioreactor. The study would improve the performance of aerobic waste treatment plants through the use of physical models and the data from physical models to calibrate and verify mathematical models.

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