Application of response surface methodology (RSM) for optimization of removal of nickel and lead from petroleum wastewater

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ABSTRACT

The Design expert version 6.0.8 was used for response surface methodology analysis.The correlation coefficients of determination (R^2)for the developed models show that the actual data fitted well with the predicted data calculated from the models. The results indicate that at optimum conditions of 1.28g/50ml of Blend 3 dose, 20mins contact time and pH of 10.35, that 97.9908% nickel and 94.234% lead could be achieved. The petroleum wastewater treated at these conditions was compared to the raw sample and it showed a marked decrease in the concentration of the specified metals far below the standard limits set by NESREA and FEPA.

Keywords: Zeolite;Crude Oil;Petroleum wastewater; Sorption, Pollution;Heavy metals.

INTRODUCTION

The refinery being an industrial plant creates a lot of polluted water containing inorganic pollutants from waste water associated with crude and reactions of production (Isehunwa, 2011). These metals can be dangerous to nerves, liver and bones and can even block functional groups of vital enzymes. Due to rapid development of industrial activities in recent years, the levels of heavy metals in water system have substantially increased over time. Among other metal ions, the ions of Ni, Cd, Mn, Zn, Hg, Pb, Cr, Cu, etc. gain importance due to their high toxic nature even at very low concentrations (Mudi, 2010).. According to Dhiraj et al 2008, conventional treatment technologies for the removal of these toxic metals are not economical and further generate huge quantities of toxic chemical sludge. Currently, various technological methods of handling these pollutants in wastewater have emerged. And the ability to optimize these technical processes yields to higher efficiency of the entire system, thus RSM is one of the vital tools for optimization of process variables. According to Helen (2009), it is a useful optimization tool for separation processes using lesser number of experimental runs planned according to RSM generated experimental design. It is useful in the study of interaction of the various parameters affecting the process (Jolanta *et al*, 2006). The RSM was done using Design - Expert 6.0.8 program. Box – Behnken response surface was adopted because it required fewer treatment combinations than central composite design in cases involving 3 or 4 factors. The Box-Behnken design is rotatable and this property prevents a potential loss of data and it requires 3 levels for each factor by producing a centerpoint. This involves; designing of experiment to provide adequate and reliable measurement of the response, developing a mathematical model having a best fit to the data obtained from the experimental design, determining the optimal values of the independent variables that produces a maximum response. (Gokhale*et al,* 2009).

MATERIALS AND METHODS

Zeolite and Kaolin (Materials)

Processing of Zeolite and Kaolin

The commercial zeolite 4A as depicted in Figure 2.1a

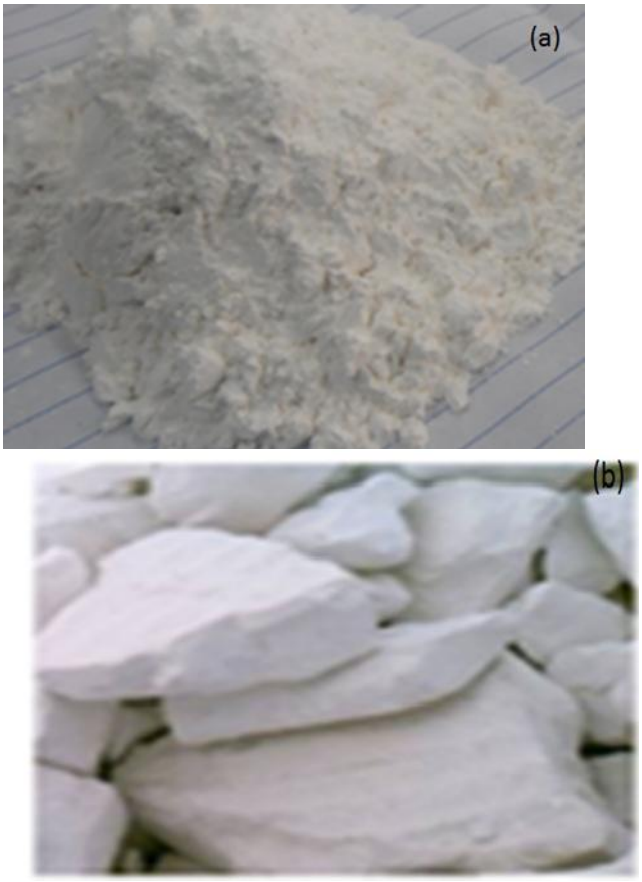

Figure 2.1(a) Zeolite 4A and (b) Raw Kaolin

was purchased from UOP, a subsidiary of Honeywell group of companies New Jersey, USA while the kaolin Figure 2.1b was procured from Kankara village in katsina state.

Beneficiation of Kaolin

About 2kg of white kaolinite clay was procured from Kankara village in Katsina state of Nigeria. This was mixed with 10litres of tap water to form slurry and was allowed to age for four days. On each day of sedimentation, decantation of the overflow was done and replaced with fresh tap water, until the last day when the overflow had become clear and free from suspended particles. The thick slurry was sieved with cloth and carefully spread out to dry at atmospheric condition. The now beneficiated kaolin was gathered and stored. The lumped kaolin clay (cake) was milled with a ball mill and sieved with a 150µm mesh.

Calcination of kaolin: The powered dried kaolin was placed in locally fabricated crucibles and charged into an already heated furnace at 750^{o}C for 3 hours where according to Ugal *et al* (2010), decomposition occurred leading to the destruction of the structure and removal of the undesirable volatile matter. By this process, kaolin was converted to metakaolin.

Conditioning of metakaolin to sodium base

The conditioning was done with 8M NaOH solution which was prepared by dissolving 400g of sodium hydroxide pellets in1250ml of deionized water. 300g of metakaolin was added to 1.5litres of the 8M NaOH and well mixed to form slurry. The mixture was then heated up to 90^{o}C with continuous vigorous stirring for 4 hours. The slurry was allowed to cool for several hours, washed for about 5 times, allowed to settle overnight, oven dried at 110^{o}C to a moisture content of about 95%, packed and stored.

Particle size analysis and blending: Particle size analysis for both the commercial zeolite 4A and sodium base metakaolin was carried out by ball milling and sieving with the same mesh of aperture 150µm, to ensure similar particle size distribution.A weight ratio of 25% zeolite 4A and 75% metakaolin were mixed and properly blended with a domestic blender (Nakai, Japan, model no. 462) to ensure homogeneityof the resultingzeolites 4A – metakaolin matrix.

Determination of Effect of Parameters on Adsorption Capacity

Accurate measurement of the specified values for Blend dose, contact time and pH as specified in Box-Benhken

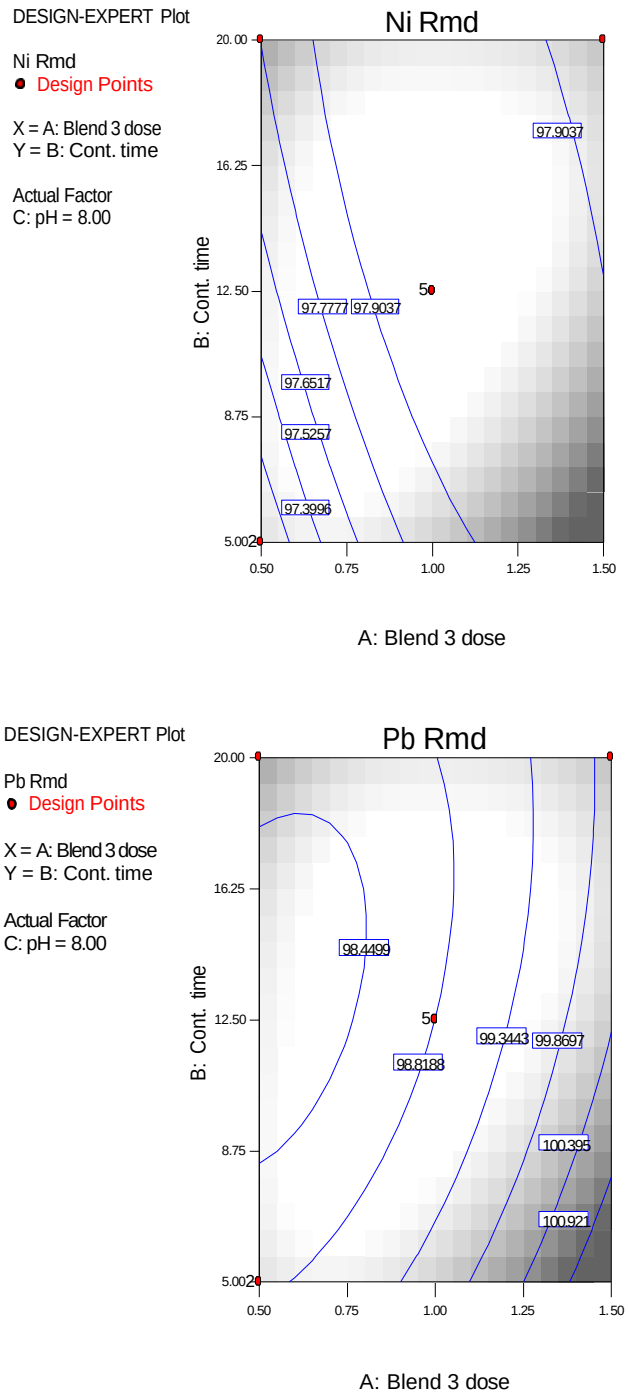

Figure. 3.1 a and b The contour diagram for Nickel, Lead

design of experimentwere dispensed separately into each of 250ml Erlenmeyer flasks petroleum wastewater samples. 50ml of the petroleum wastewater samples were added to the content of the flasks in turn and stoppered. This was followed by agitation at constant speed. The mixtures in each flask were filtered by suction pump through a sintered glass crucible andthe different filtrates were collected and analyzed using Atomic Absorption Spectrophotometer for concentration of nickel and lead in ppm.

Response Surface methodology (RSM)

The parameters affecting the removal of nickel, lead from petroleum wastewater was studied using data generated from Box – Benhken experimental design. The three

Table 3.1 : DOE for Optimization by Response Surface methodology (RSM)

Std	Run	Block	x_1 g/50ml	x_2 mins	x_3	y_{Ni} %	y_{Pb} %
8	1	Block 1	0.5	5	8	97.0224	99.0182
15	2	Block 1	0.5	5	8	97.7260	98.8118
4	3	Block 1	1	20	12	98.7006	87.3896
2	4	Block 1	1	5	12	98.2135	88.4229
6	5	Block 1	1.5	12.5	4	99.4316	99.5341
16	6	Block 1	1	12.5	8	97.8343	98.9666
1	7	Block 1	1.5	20	8	97.5638	99.6905
11	8	Block 1	0.5	20	8	97.7804	98.6038
12	9	Block 1	1	5	4	99.0254	99.0182
9	10	Block 1	1	20	4	99.2964	99.1730
7	11	Block 1	1	12.5	8	97.7804	98.1396
17	12	Block 1	1	12.5	8	98.0508	99.4825
5	13	Block 1	1	12.5	8	98.1591	98.9150
14	14	Block 1	0.5	12.5	12	98.7005	86.3562
13	15	Block 1	0.5	12.5	4	98.0508	98.5007
3	16	Block 1	1	12.5	8	98.1591	98.6038
10	17	Block 1	1.5	12.5	12	98.3488	90.1286

Notation:
X_1= Blend dose
X_2=Contact time
X_3= pH
yNi= Percentage nickel removed
yPb= Percentage lead removed

Table 3.2: Sequential Model Sum of Squares: Response: Ni, Pb, Cd, Mn Removed.
(a) Nickel

Source	**Sum of squares**	**DF**	**Mean Square**	**F Vaue**	**Prob>F**	
Mean	1.640E+005	1	1.640E+005			Suggested
Linear	1.31	3	0.44	1.10	0.3853	
2FI	1.78	3	0.59	1.76	0.2185	
Quadratic	2.74	3	0.91	10.04	0.0063	Suggested
Cubic	0.26	0.13	1.73	0.2688		Aliased
Residual	0.38	5	0.075			
Total	1.640E+005	17	9648.75			

Lead

Source	Sum of squares	DF	Mean Square	F Vaue	Prob>F	
Mean	1.580E+005	1	1.580E+005			
Linear	241.36	3	80.45	7.98	0.0029	Suggested
2FI	13.22	3	4.41	0.37	0.7739	
Quadratic	116.39	3	38.80	182.32	<0.0001	Suggested
Cubic	0.49	2	0.24	1.22	0.3696	Aliased
Residual	1.00	5	0.20			
Total	1.583E+005	17	9314.36			

independent variables were coded as contact time (CT), Matrix dose (MD)and pH respectively. The nickel and lead removed were also coded as Ni Rmd and Pb Rmd.

A total of 17 experimental runs were carried out according to the experimental design matrix shown in figure 3.1 and the percentage nickel and lead removed were determined using atomic absorption spectrophotometer (AAS) (Martins et al, 1994) as described in section 2.2. Analysis of the results were done applying coefficient of determination (R^2) and

Table 3.3. The Model fit Summary for (a) Nickel and (b) Lead

(a) Nickel

Source	Std. Dev.	R-Squared	Adjusted R-Squared	Predicted R-Squared	PRESS	
Linear	3.175623	0.64802	0.566794	0.348124	242.7998	Suggested
2FI	3.433386	0.683509	0.493614	-0.25729	468.2946	
Quadratic	0.461302	0.996001	0.990859		+	Suggested
Cubic	0.447304	0.997314	0.991405		+	Aliased

(b) Lead

Source	Std. Dev.	R-Squared	Adjusted R-Squared	Predicted R-Squared	PRESS	
Linear	0.629809	0.202034	0.017888	-0.55392	10.04169	
2FI	0.581044	0.477554	0.164087	-1.29009	14.79888	
Quadratic	0.30159	0.901473	0.774796		+	Suggested
Cubic	0.274379	0.94175	0.813601		+	Aliased

response plots and a mathematical model was generated for the process.

RESULTS AND DISCUSSION

Model equations for nickel, lead;
Final Equations in terms of Actual Factors

$$y_{Ni} = 98.24919 + 4.55040x_1 + 0.071753x_2 - 0.74420x_3 - 0.97818x_1^2 - 1.21809E^{-003}x_2^2 + 0.055046x_3^2 - 0.043846x_1.x_2 - 0.21657x_1.x_3 + 1.80069E^{-003}x_2.x_3 \quad (1)$$

$$y_{Pb} = 89.35916 - 3.66843x_1 - 0.055691x_2 + 4.10711x_3 + 2.02752x_1^2 + 6.71848E^{-003}x_2^2 - 0.35616x_3^2 - 0.084979x_1.x_2 + 0.34239x_1.x_3 - 9.90132E^{-003}x_2.x_3 \quad (2)$$

Refined Equations in terms of Actual Factors

$$y_{Ni} = 98.24919 + 0.055046x_3^2 - 0.21657x_1.x_3 \quad (3)$$

The model fit summary in Table 3.3 shows that quadratic model is the suggested selected model with adjusted R^2 of 0.9909 and predicted R^2 of 0.3481. This value is higher than -0.55392 and -1.29009 values respectively obtained for linear model. This shows that adding the quadratic (squared) terms to the mean, block, linear and two factor interaction terms already in the model is significant. For each source of terms (linear, quadratic and cubic) as depicted in Table 3.2, the probability ("PROB > F") was examined to see if it falls below 0.05. So far, the quadratic model looks best – these terms are significant, but adding the cubic other terms will not significantly improve the fit since it is aliased.

The word lack of fit refers to the fact that the simple linear regression model may not adequately fit the data. If

Optimization by Response Surface Method (RSM)

RSM was used to optimize the adsorption parameters of removing nickel and lead from petroleum wastewater as indicated in table 3.1.

$$y_{Pb} = 89.35916 - 3.66843x_1 + 4.10711x_3 + 2.02752x_1^2 - 0.35616x_3^2 + 0.34239x_1.x_3 \quad (4)$$

Where,

$y_{Ni} = Nickel\ Removed$

$x_1 = A = Blend\ dose$

$y_{Pb} = Lead\ Removed$

$x_2 = B = Contact\ time$

$x_3 = C = pH$

Table 3.1 presents the design of experiment (DOE) and the responses indicating that nickel and lead are measurable heavy metals.
the SS for lack of fit is small, there is evidence that the simple regression model is more appropriate to explain the relationship of the parameter (Prasad, 2002). The "Lack of Fit Tests" shown in Table 3.4 compares the residual error to the "Pure Error" from replicated design points. In this case, the linear model definitely can be ruled out, because it's Prob > F falls below 0.05. The quadratic model, identified earlier as the likely model, does not show significant lack of fit. Since the cubic model is aliased, so it cannot be chosen for model prediction. The "Model Summary Statistics" Table 3.4 lists other statistics useful in comparing models. The quadratic model comes out best: It exhibits low standard deviation ("Std. Dev.") value of 0.2, high "R-Squared" value of 0.9908 for Ni and 0.9015 for Pb.

Table 3.4. Lack of Fit Tests for the Process
Nickel

Source	Sum of squares	DF	Mean Square	F Vaue	Prob>F	
Linear	4.78	8	0.60	7.94	0.0177	
2FI	3.00	5	0.60	7.97	0.0199	
Quadratic	0.26	2	0.13	1.73	0.2688	Suggested
Cubic	0.00	0				Aliased
Pure Error	0.38	5	0.075			

(b) Lead

Source	Sum of squares	DF	Mean Square	F Vaue	Prob>F	
Linear	130.10	8	16.26	81.28	<0.0001	
2FI	116.88	5	23.38	116.83	<0.0001	
Quadratic	0.49	2	0.24	1.22	0.3696	Suggested
Cubic	0.00	0				Aliased
Pure Error	1.00	5	0.20			

"Lack of Fit Tests": Want the selected model to have insignificant lack-of-fit.

Table 3.5. ANOVA for Response Surface Quadratic Model for Ni, Pb, Cd and Mn

(a) Nickel

Source	**Sum of Squares**	**DF**	**Mean Square**	**F Value**	**Prob> F**	
Model	5.83	0.2020	0.0179	-0.5539	10.04	significant
A	*0.14*	*1*	*0.14*	*1.51*	*0.2586*	
B	*0.044*	*1*	*0.044*	*0.49*	*0.5077*	
C	*0.42*	*1*	*0.42*	*4.66*	*0.0678*	
A^2	*0.21*	*1*	*0.21*	*2.26*	*0.1766*	
B^2	*0.016*	*1*	*0.016*	*0.18*	*0.6863*	
C^2	*2.66*	*1*	*2.66*	*29.30*	*0.0010*	
AB	*0.058*	*1*	*0.058*	*0.64*	*0.4499*	
AC	*0.75*	*1*	*0.75*	*8.25*	*0.0239*	
BC	*0.012*	*1*	*0.012*	*0.13*	*0.7307*	
Residual	*0.64*	*7*	*0.091*			
Lack of Fit	*0.26*	*2*	*0.13*	*1.73*	*0.2688*	*not significant*
Pure Error	*0.38*	*5*	*0.075*			
Cor Total	6.46	16				

Lead

Source	**Sum of Squares**	**DF**	**Mean Square**	**F Value**	**Prob> F**	
Model	370.97	9	41.22	193.70	<0.0001	significant
A	*5.96*	*1*	*5.96*	*28.01*	*0.0011*	
B	*0.85*	*1*	*0.85*	*3.99*	*0.0859*	
C	*241.21*	*1*	*241.21*	*1133.53*	*<0.0001*	
A^2	*0.88*	*1*	*0.88*	*4.15*	*0.0811*	
B^2	*0.49*	*1*	*0.49*	*2.31*	*0.1727*	
C^2	*111.56*	*1*	*111.56*	*524.26*	*<0.0001*	
AB	*0.22*	*1*	*0.22*	*1.03*	*0.3444*	
AC	*1.88*	*1*	*1.88*	*8.81*	*0.0208*	
BC	*0.35*	*1*	*0.35*	*1.66*	*0.2387*	
Residual	*1.49*	*7*	*0.21*			
Lack of Fit	*0.49*	*2*	*0.24*	*1.22*	*0.3696*	*significant*
Pure Error	*1.00*	*5*	*0.20*			
Cor Total	372.46	16				

The ANOVA in Table 3.5 confirms the adequacy of the quadratic model (the Model Prob>F is less than 0.05.)The Model F-value of 16.71 implies the model is significant. There is only a 0.06% chance that a "Model F-Value" this large could occur due to noise.Values of "Prob > F" less than 0.0500 indicate model terms are significant. In this case A, C, AC, A2, C2 are significant model terms. Values greater than 0.1000 indicate the model terms are not significant. If there are many insignificant model terms (not counting those required to support hierarchy), model reduction may improve your model.

Table 3.6 a, b. Diagnostic Case Statistics for Nickel, Lead

(a) **N**ickel

Standard Order	Actual Value	Predicted Value	Residual
1	97.5638	97.7649	-0.2011
2	98.21352	98.43589	-0.22237
3	98.15913	97.99675	0.162381
4	98.70056	98.72183	-0.02127
5	98.15913	97.99675	0.162381
6	99.43162	99.45289	-0.02127
7	97.78037	97.99675	-0.21638
8	97.02236	97.27362	-0.25126
9	99.29638	99.07401	0.222374
10	98.34875	98.12638	0.222374
11	97.78037	97.78037	0
12	99.02542	99.00415	0.021271
13	98.05084	98.27322	-0.22237
14	98.70056	98.67929	0.021271
15	97.72598	97.27362	0.452361
16	97.83427	97.99675	-0.16248
17	98.05084	97.99675	0.054094

Lead

Standard Order	Actual Value	Predicted Value	Residual
1	99.69048	100.03	-0.33947
2	88.42294	88.69627	-0.27333
3	98.60383	98.82149	-0.21766
4	87.38955	87.3234	0.066147
5	98.91502	98.82149	0.093522
6	99.53406	99.46791	0.066147
7	98.13955	98.82149	-0.68194
8	99.01819	98.74528	0.27291
9	99.17295	98.89962	0.273326
10	90.12863	89.85531	0.273326
11	98.60383	98.60383	0
12	99.01819	99.08434	-0.06615
13	98.50066	98.77398	-0.27333
14	86.35615	86.4223	-0.06615
15	98.81184	98.74528	0.066563
16	98.9666	98.82149	0.145108
17	99.48247	98.82149	0.660975

Figure. 3.2 a and b Residual Plot for Nickel and Lead

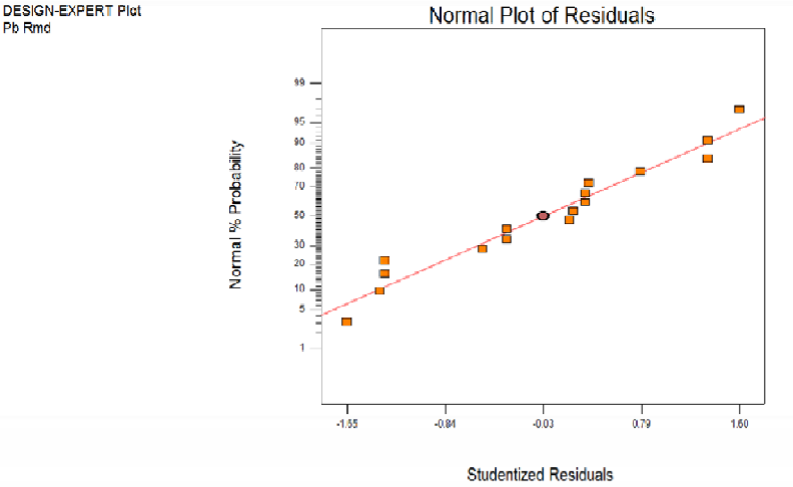

Figure. 3.2 a and b Residual Plot for Nickel and Lead

Table 3.7.The Optimized RSM Values

Name	Goal	Lower Limit	Upper Limit	Lower Weight	Upper Weight	Importance
Blend 3 dose	maximize	0.5	1.5	1	1	3
Cont. time	maximize	5	20	1	1	3
pH	maximize	4	12	1	1	3
Ni Rmd	maximize	97.0224	99.4316	1	1	3
Pb Rmd	maximize	86.3561	99.6905	1	1	3

No.	Blend 3 dose	Cont. time	pH	Ni Rmd	Pb Rmd	Desirability	
1	1.28	20.00	10.35	97.9908	94.234	0.757	Selected
2	1.26	20.00	10.37	98.0194	94.1081	0.757	

Table 3.8. Quality of the Petroleum Wastewater Before and After Treatment.

Metals	Petroleum Wastewater Before Treatment	Petroleum wastewater After Treatment	*Drinking water Quality standard (NESREA)
Ni (mg/l)	0.040	0.000	0.0100
Pb(mg/l)	0.225	0.020	0.0100
Cd(mg/l)	0.022	0.001	0.003
Mn (mg/l)	1.823	0.001	0.200

*National Environmental Standards and Regulations Enforcement Agency (NESREA, 2010)

The "Lack of Fit F-value" of 1.73 as depicted in Table 3.5 implies the Lack of Fit is not significant relative to the pure error. There is a 31.47% chance that a "Lack of Fit F-value" this large could occur due to noise. Non-significant lack of fit is good -- we want the model to fit.

The "Pred R-Squared" of 0.3481 is not as close to the "Adj R-Squared" of 0.9914 as one might normally expect. This may indicate a large block effect . A ratio greater than 4 is desirable. The ratio of 16.415 indicates an adequate signal. This model can be used to navigate the design space.

The important diagnostic tool used as depicted in Table 3.6 is the normal probability plot of the studentized residuals shown in Figure 3.2. The data points from the plot is approximately linear, which shows that the quadratic model developed is a good representation o the process.

In the contour plot for the model graph shown in Figure 3.1, a plot of Ni and Pb uptake as a function of contact time and adsorbent dose at a mid-level slice of initial concentration. This slice includes five centerpoints as indicated by the dot at the middle of the contour plot. By replicating center points, a very good power of prediction at the middle of experimental region can be obtained.

Figures 3.2 shows the plot of the predicted versus actual experimental values showing that the actual values are distributed relatively near the straight line. This

indicates that the models are adequate for predicting the efficiency within the range of the variables studied (Prasad, 2002). Thus Table 3.7 indicates the optimized values of 1.28g/50mL Blend 3 dose, 20minutes Contact time between the adsorbent and the adsorbate and pH of 10.35 indicating an alkali medium to achieve 98% nickel and 945 lead uptake.

The concentrations before and after treatment for the petroleum wastewater presented in Table 3.8 indicates that the heavy metals were removed even far beyond the threshold limits of NESREA, indicating the appropriateness of the prepared Blend and the generated models and their suitability for field applications.

CONCLUSION

The RSM proved to be a useful optimization tool for this process. The validated models developed fitted well with the experimental data indicating a high precision model. The generalized developed model could be used in similar application of wastewater treatment except that some pre-treatments could be done like digestion of the samples could be carried out to loosen the bonds and complexes of the metals in the wastewater sample. The pollution loadings of the petroleum wastewater was reduced far below the standards set by NESREA.

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