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OPTIMIZATION OF PROCESS PARAMETERS IN TREATMENT OF BREWERY EFFLUENT

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Abstract: A three– variable Box–Behnken design (BBD) coupled with response surface methodology (RSM) was employed to optimize and evaluate the effect of adsorbent dose, contact time and temperature on percentage reduction of BOD, COD and TDS in brewery effluent. Adsorbent was prepared from coconut shell, which was carbonized at temperature of 600°C for 2 hours and thereafter activated. The effluent was treated with the adsorbent by varying three variables: adsorbent dosage (1–5 g), contact time (40–180) and temperature (30–40°C). Statistical analysis of the results showed that all the factors, except the temperature, had significant effect on the responses Quadratic models were developed for percentage reduction of (biological oxygen demand) BOD, chemical oxygen demand (COD) and total dissolved solids (TDS). The models were significant with $p < 0.0001$ and showed a good fit to the experimental data. The percentage reduction of BOD, COD and TDS were positively influenced by adsorbent dose and contact time. The temperature range used for this study did not have so much effect on the responses. The optimum conditions for BOD, COD and TDS reduction of 75.268%, 69.865% and 69% respectively were adsorbent dosage of 5g, contact time of 180 minutes and temperature of 34.4°C.
Keywords: brewery effluent; BBD; adsorbent; optimization

INTRODUCTION

The industrialization of developing countries has led to increased industrial activities. A major source of pollution in developing countries is industrial activities and this has gradually increased the problem of waste disposal (Alao *et al.*, 2010). The emerging industries include metal plating, mining, painting, and brewery.

Brewery wastes are composed mainly of liquor pressed from the wet grain and wash water from the various departments (Noorjahan and Jamuna, 2012). Untreated wastes from processing factories located in cities are usually discharged into inland water bodies. The resultant water pollution poses demonstrated risks to aquatic ecosystems, human health and productive activities (UNEP, 2016). The Biochemical oxygen demand levels of brewery effluents are quite high, as are the total solids; typically about half the BOD and over 90% of the suspended solids are generated in the brewing operation (Noorjahan and Jamuna, 2012). Disposal of such effluent without any prior treatment into water courses causes serious pollution problems (Ninnekar, 1992).

A number of treatment methods for industrial effluents have been reported, which includes, ion exchange, electrodialysis, electrochemical precipitation, evaporation, solvent extraction, reverse osmosis, chemical precipitation and adsorption (Gupta *et al.*, 2009). Most of these methods suffer from drawbacks such as high capital and operational costs or the disposal of the residual sludge. Due to its simplicity and easy operational conditions, adsorption is a widely–used process (Mabrouk et al., 2009).

In studying the individual and interactive effects of the selected effluent parameters on the chosen responses, a statistical design of experiments is employed as against the traditional one–factor–at–a–time experiment which is time–consuming (Carmona *et al*, 2005; Huang *et al.*, 2008). Response surface methodology based on statistically designed experiments has been found to be very useful in optimising multivariable processes.

The aim of this study was to optimise the effect of adsorbent dose, contact time and temperature on the percentage reduction of COD, BOD and TDS of brewery effluent. A three variable BBD was adopted to design the percentage reduction of the selected effluent physicochemical parameters.

METHODOLOGY

— Preparation of Activated Carbon and Carbonization

The coconut shells were obtained waste bins at Uselu market in Benin City, Edo state. Coconut fibre and sand were removed from the shells and washed with water, to remove dust and other impurities, sun dried and were pulverised. The pulverized coconut shells was carbonized at 600°C for 2 hours and allowed to cool. It was then impregnated in 100 mL 20% (v/v) concentration of phosphoric acid for 24 hours. The sample was washed with distilled water until a pH of 6–7 was obtained and then the sample was dried to remove moisture at 85°C for 2 hours in the oven. The dried activated carbon was crushed with a mortar and sieved using a 35 mesh size to obtain a particle size of 0.45 mm or less.

— Effluent Collection

Samples of effluents were collected at point of discharge from a brewery in Benin City, Nigeria. They were collected in 2 L sterile glass bottles and transported to the laboratory at 4°C for analysis.

— Effluent Characterization

The TDS of effluents was determined by using ELICO EC–TDS meter (CM 183) where electrode was directly dipped into the respective solutions to display result on a digital scale. Biochemical oxygen demand (BOD) was determined according to standard Methods for the examination of water and waste water (APHA, 2005).

COD determination was carried out with dichromate reflux method with the addition of 10 ml of 0.25 N potassium dichromate ($K_2Cr_2O_7$) and 30 ml H_2SO_4+Ag_2SO_4 reagent in 20 ml diluted sample. The mixture was refluxed for 2 h and was cooled to room temperature. The solution was then diluted to 150 ml by using distilled water and excess $K_2Cr_2O_7$ remained was titrated with ferrous ammonium sulphate (FAS) using ferroin indicator.

$$\mathrm{COD} = \frac{(\mathrm{A-B})*\mathrm{N}*1000*8}{\text{volume of sample}} \quad (1)$$

where *A* is the ml of FAS used for blank; *B* is the ml of FAS used for sample, *N* is the normality of FAS and 8 is milliequivalent weight of oxygen.

— Experimental Design

A three variable Box–Behnken design (BBD) for response surface methodology was used to develop a statistical model for the reduction of BOD, COD and TDS of effluent. The ranges of the variables that were optimized are as shown in Table 1. The experimental design made up of 17 runs was developed using Design Expert 7.0.0 (Stat–ease, Inc. Minneapolis, USA). The levels of the independent variables as shown in Table 1 were selected based on preliminary experiments. The relation between the coded values and actual values are described as follows:

$$x_i = \frac{X_i - X_0}{\Delta X} \quad (2)$$

where x_i and X_i are the coded and actual values of the independent variable respectively. X_o is the actual value of the independent variable at the centre point and ΔX_i is the step change in the actual value of the independent variable.

Table 1: Experimental range and levels of independent variables

Independent Variables	Symbols	Coded and Actual Levels		
		−1	0	+1
Adsorbent dose (g)	X_1	1	3	5
Contact time (min)	X_2	40	110	180
Temperature (°C)	X_3	30	35	40

RESULTS AND DISCUSSION

Experiment was conducted at different levels of combination of factors that affect adsorption (adsorbent dose, contact time and temperature), using statistically designed experiment. The data obtained was analyzed by RSM (response surface methodology), and the results were presented using suitable graphs.

Linear, cubic and quadratic models were investigated by the software to select the statistically significant model for determining the relationship between the responses and the input variables. The statistics of the models summaries for the four responses are given in Table 3–5.

Table 2: Three level factorial Box–Behnken design matrix and the experimental responses

Run No.	Factors			Responses		
	X_1	X_2	X_3	BOD (Y_1) Actual	COD (Y_2) Actual	TDS (Y_3) Actual
1	3	110	35	73.082	66.335	66.257
2	1	180	35	52.899	59.605	54
3	5	110	30	74.995	69.084	69
4	1	110	30	51.761	57.554	53.333
5	3	180	40	73.785	68.667	67
6	1	40	35	50.1	57.081	53.333
7	3	180	30	72.586	68.751	67.289
8	3	40	40	69.348	66.297	65.425
9	3	110	35	72.264	67.899	66.667
10	3	40	30	69.995	64.775	64.235
11	5	40	35	73.998	68.1	68.085
12	3	110	35	71.896	68.364	65
13	3	110	35	72.002	67.096	65.25
14	5	110	40	74.005	68.995	67
15	1	110	40	52.387	57.005	54
16	3	110	35	72.347	67.45	63.333
17	5	180	35	75.028	69.125	68.5

Table 3: Model summary statistics for BOD

Source	Std. dev	R–Squared	Adjusted R–Squared	Predicted R–Squared	F Value	
Linear	5.06	0.7588	0.7031	0.5673	13.63	
2FI	5.75	0.7605	0.6167	0.0693	0.023	
Quadratic	0.59	0.9982	0.9960	0.9810	316.10	Suggested
Cubic	0.47	0.9994	0.9975		2.40	Aliased

Table 4: Model summary statistics for COD

Source	Std. Dev	R–Squared	Adjusted R–Squared	Predicted R–Squared	F Value	
Linear	2.38	0.7760	0.7243	0.5973	15.01	
2FI	2.69	0.7799	0.6478	0.1438	0.058	
Quadratic	0.85	0.9847	0.9650	0.8606	50.02	Suggested
Cubic	0.78	0.9927	0.9707		1.46	Aliased

Table 5: Model summary statistics for TDS

Source	Std. Dev	R–Squared	Adjusted R–Squared	Predicted R–Squared	F–Value	
Linear	2.86	0.7998	0.7536	0.6264	2.893	
2FI	3.22	0.8043	0.6868	0.1831	0.563	
Quadratic	1.13	0.988	0.9612	0.9124	45.05	Suggested
Cubic	1.3	0.9873	0.949		1.06	Aliased

From Tables 3–5, it is seen that the suggested quadratic model is satisfactory since it has the highest F values of 316.10, 50.02 and 45.05 for BOD, COD and TDS respectively. As shown in a related study (Yi *et al.*, 2010), the larger the magnitude of the F–value and correspondingly the smaller the 'Prob. > F' value, the more significant is the corresponding coefficient.

Regression analysis was performed to fit the response. Regression models were developed for each response, BOD (Y_1), COD (Y_2) and TDS (Y_3), as a function of X_1, X_2 and X_3 as shown in Equations (1)–(3).

$$\begin{gathered}Y_1 = 16.77376 + 20.53151X_1 + 0.00898969X_2 \\ +0.83339X_3 - 0.00315893X_1X_2 - 0.0404X_1X_3 \\ +0.00131857X_2X_3 - 2.18168X_1^2 \\ -0.000119434X_2^2 - 0.012179X_3^2\end{gathered} \quad (1)$$

$$\begin{gathered}Y_2 = 28.24171 + 8.58117X_1 + 0.065582X_2 \\ +0.98606X_3 - 0.00267679X_1X_2 + 0.0115X_1X_3 \\ - 0.00114714X_2X_3 - 0.98926X_1^2 \\ +0.00000121939X_2^2 - 0.012491X_3^2\end{gathered} \quad (2)$$

$$\begin{gathered}Y_3 = 46.06836 + 13.10999X_1 + 0.029843X_2 \\ -0.45001X_3 - 0.00045X_1X_2 - 0.066675X_1X_3 \\ -0.00105643X_2X_3 - 1.18449X_1^2 \\ +0.0000849082X_2^2 + 0.010792X_3^2\end{gathered} \quad (3)$$

Statistical testing of the models was executed with analysis of variance (ANOVA) and the results are given in Tables 6–8.

Table 6: Analysis of variance of model developed for BOD

Source	Sum of squares	DF	Mean square	F Value	P–Value	
Model	1377.52	9	153.06	442.35	< 0.0001	Significant
X_1	1032.37	1	1032.37	2983.67	< 0.0001	
X_2	14.73	1	14.73	42.58	0.0003	
X_3	4.42*10−3	1	4.42*10−3	0.013	0.9132	
X_1X_2	0.78	1	0.78	2.26	0.1764	
X_1X_3	0.65	1	0.65	1.89	0.2119	
X_2X_3	0.85	1	0.85	2.46	0.1606	
X_1^2	320.66	1	320.66	926.73	< 0.0001	
X_2^2	1.44	1	1.44	4.17	0.0805	
X_3^2	0.39	1	0.39	1.13	0.3234	
Residual	2.42	7	0.35			
Lack of Fit	1.56	3	0.52	2.4	0.2086	not significant
Pure Error	0.87	4	0.22			
Cor Total	1379.94	16				

The model Fisher F–tests of 442.35, 50.02 and 45.05 with low probability value (p<0.0001) show a high statistical significance for the regression models as shown in Table 6–8[10]. The "Lack of Fit F–values" of 2.4, 1.46 and 0.44 and P–values of 0.2086, 0.3521 and 0.7355 imply the Lack of Fit is not significant relative to the pure error.

A non–significant lack of fit is desirable as it implies that the model could be used for theoretical prediction of the reduction of BOD, COD and TDS (Vazquez *et al.*, 2011). The R^2 values of 0.9960, 0.9650 and 0.988 imply that the predicted values were found to be in good agreement with experimental values (Khataee *et al.*, 2010). A regression model is well defined if R^2 value is higher than 0.80 (Sin *et al.*, 2006). Response surface curves were generated from the statistical models to examine the interactions between the independent variables and to determine the optimum levels of the variables.

The effects of adsorbent dosage, contact time and temperature on BOD reduction, COD reduction and TDS reduction as responses are shown in the response surface graphs given in Figure 1–9.

Table 7: Analysis of variance of model developed for COD

Source	Sum of squares	DF	Mean square	F Value	P–Value	
Model	323.53	9	35.95	50.02	< 0.0001	Significant
X_1	242.65	1	242.65	337.64	< 0.0001	
X_2	12.24	1	12.24	17.03	0.0044	
X_3	0.08	1	0.08	0.11	0.7484	
X_1X_2	0.56	1	0.56	0.78	0.406	
X_1X_3	0.053	1	0.053	0.074	0.794	
X_2X_3	0.64	1	0.64	0.9	0.3751	
X_1^2	65.93	1	65.93	91.74	< 0.0001	
X_2^2	1.5* 10−4	1	1.5* 10−4	2.09* 10−4	0.9889	
X_3^2	0.41	1	0.41	0.57	0.4744	
Residual	5.03	7	0.72			
Lack of Fit	2.63	3	0.88	1.46	0.3521	not significant
Pure Error	2.4	4	0.6			
Cor Total	328.56	16				

Table 8: Analysis of variance of model developed for TDS

Source	Sum of squares	DF	Mean square	F Value	P–Value	
Model	520.41	9	57.82	45.05	< 0.0001	Significant
X_1	419.33	1	419.33	326.67	< 0.0001	
X_2	4.08	1	4.08	3.18	0.1179	
X_3	0.023	1	0.023	0.018	0.8966	
X_1X_2	0.016	1	0.016	0.012	0.9146	
X_1X_3	1.78	1	1.78	1.39	0.2777	
X_2X_3	0.55	1	0.55	0.43	0.5348	
X_1^2	94.52	1	94.52	73.63	< 0.0001	
X_2^2	0.73	1	0.73	0.57	0.4757	
X_3^2	0.31	1	0.31	0.24	0.64	
Residual	8.99	7	1.28			
Lack of Fit	2.24	3	0.75	0.44	0.7355	not significant
Pure Error	6.75	4	1.69			
Cor Total	529.39	16				

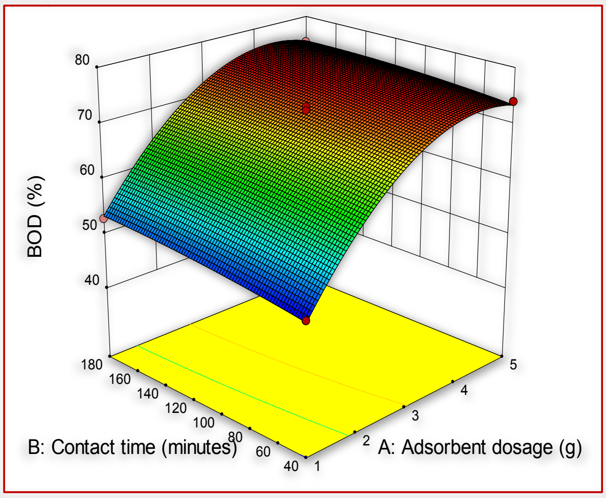

Figure 1: Response surface plot showing predicted BOD reduction as a function of adsorbent dosage and contact time with temperature fixed at 35°C.

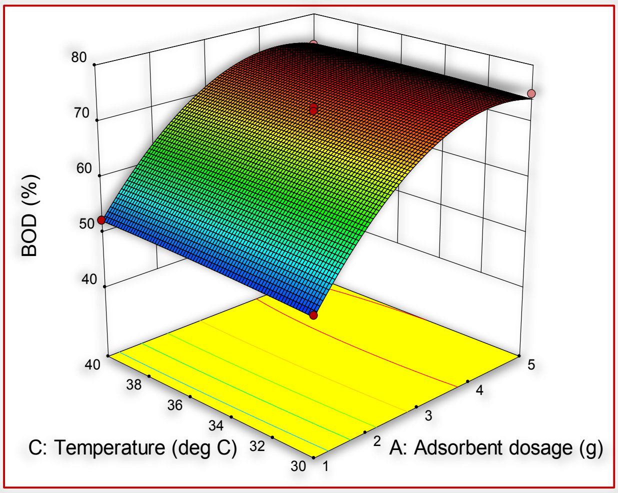

Figure 2 : Response surface plot showing predicted BOD reduction as a function of adsorbent dosage and temperature with contact time fixed at 110minutes.

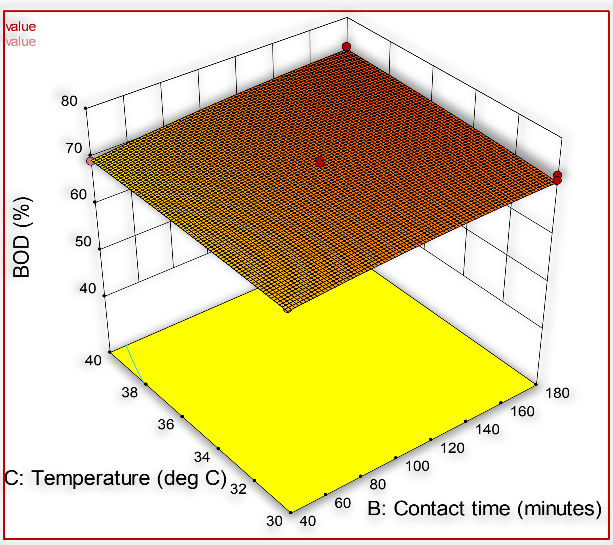

Figure 3: Response surface plot showing predicted BOD reduction as a function of contact time and temperature with fixed adsorbent dosage at 3g.

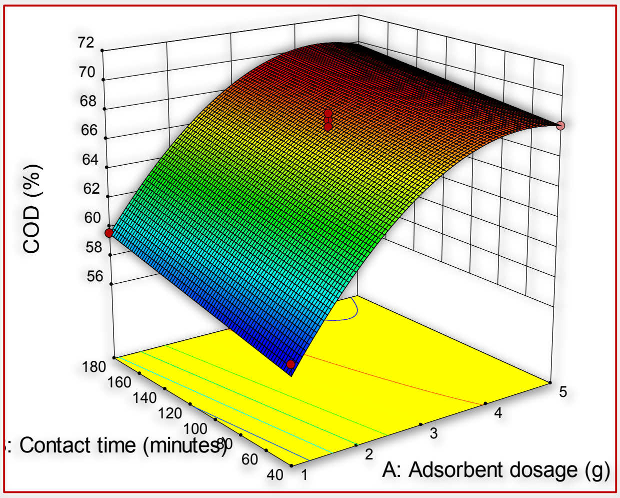

Figure 4: Response surface plot showing predicted COD reduction as a function of adsorbent dosage and contact time with temperature fixed at 35°C.

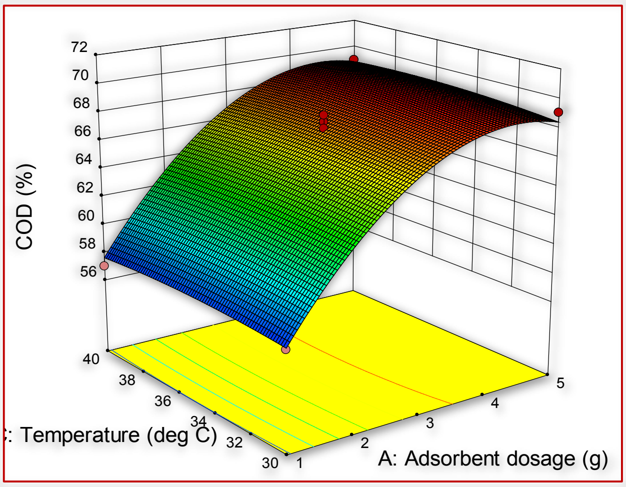

Figure 5: Response surface plot showing predicted COD reduction as a function of adsorbent dosage and temperature with contact time fixed at 110minutes.

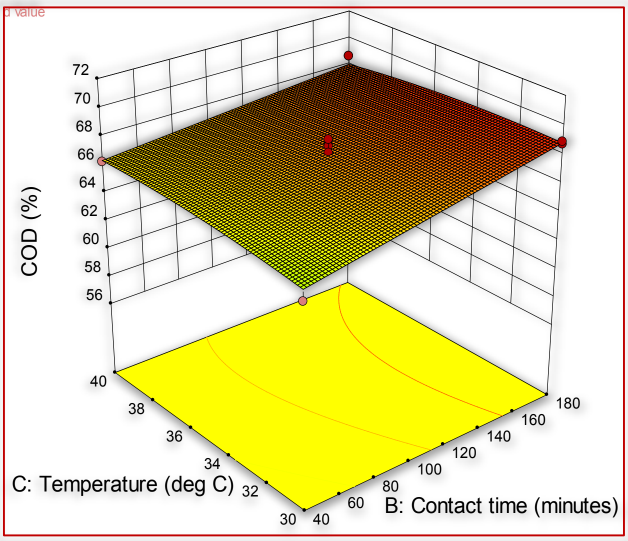

Figure 6: Response surface plot showing predicted COD reduction as a function of temperature and contact time with adsorbent dosage fixed at 3g.

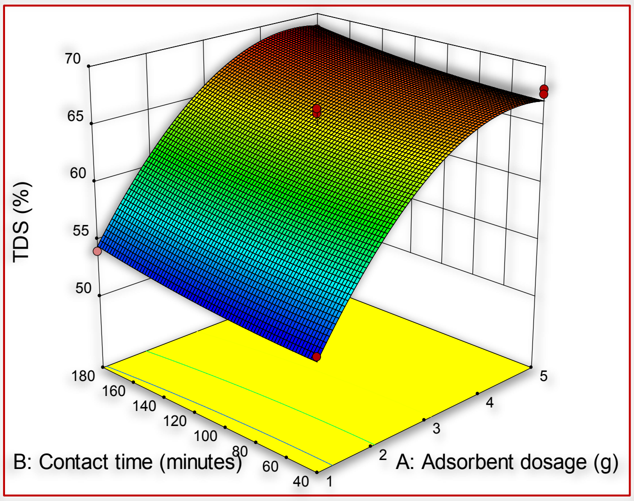

Figure 7: Response surface plot showing predicted TDS reduction as a function of adsorbent dosage and contact time with temperature fixed at 35°C.

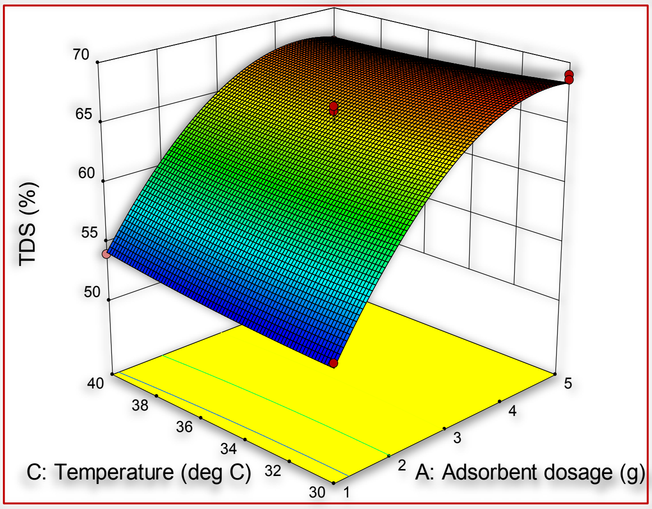

Figure 8: Response surface plot showing predicted TDS reduction as a function of adsorbent dosage and temperature with contact time fixed at 110minutes

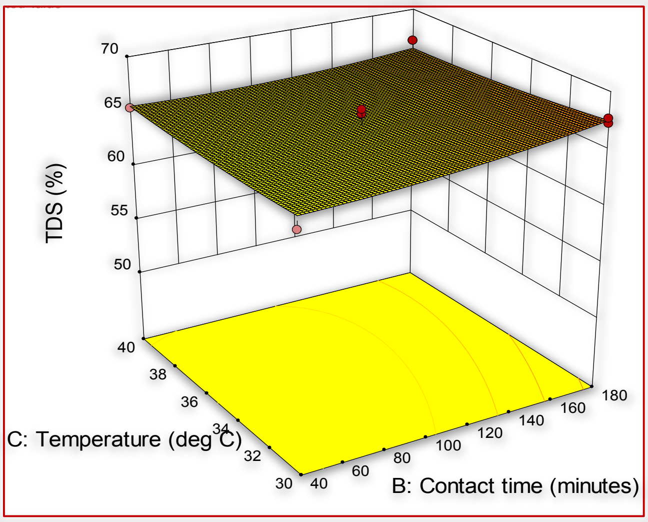

Figure 9: Response surface plot showing predicted TDS reduction as a function of contact time and temperature with adsorbent dosage fixed at 3g

From Figures 1–3 BOD removals increased as adsorbent dose, contact time and temperature increased. There was a high statistical influence of adsorbent dose on BOD reduction compared to contact time. Also BOD reduction was more affected by contact time than temperature. This is also corroborated by the fact that adsorbent dose had a much smaller p value (<0.0001) than contact time, which had a smaller p value than temperature as shown in Table 6.

From Figures 4–6, COD removal increased as adsorbent dose, contact time and temperature increased. There was a high statistical influence of adsorbent dose on COD reduction compared to contact time. Also COD reduction was more affected by contact time than temperature. This is also corroborated by the fact that adsorbent dose had a much smaller p value (<0.0001) than contact time, which had a smaller p value than temperature as shown in Table 7.

From Figures 7–9 TDS removal increased as adsorbent dose, contact time and temperature increased. There was a high statistical influence of adsorbent dose on TDS reduction compared to contact time and temperature. Also TDS reduction was more affected by contact time than temperature. This is also corroborated by the fact that adsorbent dose had a much smaller p value (<0.0001) than contact time, which had a smaller p value than temperature as shown in Table 8. As shown in Figures 2, 3, 5, 6, 8 and 9, generally temperature did not have any significant effect on BOD, COD and TDS reduction. This is corroborated by the fact that temperature had high p–values of 0.9132, 0.7484 and 0.8966 as shown in Tables 6–8.

The values of adsorbent dose, contact time and temperature were optimized based on the statistical models. The highest BOD, COD and TDS percentage reduction of 75.268%, 69.865% and 69% respectively at optimum adsorbent dose of 5 g, contact time of 180 min and temperature of 34.4°C.

The validity of the results predicted by the regression models, were confirmed by carrying out triplicate experiments under optimal conditions (that is adsorbent dose of 5 g, contact time of 180 min and temperature of 34.4°C).

The results obtained from three replications demonstrated that the average of percentage reductions of 74.98%, 69.78% and 68.99 % for BOD, COD and TDS respectively were close to the predicted percentage reduction values of 75.268%, 69.865% and 69% for BOD, COD and TDS respectively. The excellent correlation between the predicted and measured values after optimization justified the validity of response models.

CONCLUSION

In this study the reduction of BOD, COD and TDS of brewery effluent using activated carbon from coconut shell as absorbent was investigated. A three–variable Box–Benhken design was used to study the simultaneous effects of adsorbent dose, contact time and temperature on reduction of BOD, COD and TDS of brewery effluent. The models developed to describe relationship among reduction of BOD, COD and TDS and the chosen independent variables were statistically significant (p<0.0001). From the RSM, the optimum values of variables were: 5 g for adsorbent dose, 180 min for contact time of 180 min and 34.4°C for temperature. The reduction of BOD, COD and TDS were generally favoured by increased adsorbent dose, contact time and, not so significantly, by temperature.

References

[1] Alao, O., Arojojoye, O., Ogunlaja, O. and Famuyiwa, A: Impact assessment of brewery effluent on water quality in Majawe, Ibadan, southwestern Nigeria, Researcher, vol. 2(5), pp. 21–28, 2010.
[2] American Public Health Association–APHA .Standard methods for the examination of water and waste, 20th ed., Washington, D.C USA, APHA –AWWA– WPCF, 2005.
[3] Carmona, M.E.R., da Silva, M.A.P. and Leite, S.G.F: Biosorption of Chromium using Factorial Experimental Design, Process Biochemistry, vol. 40, pp. 779–788, 2005.
[4] Gupta, N., Prasad, M., Singhal, N. and Kumar, V: Modeling the Adsorption Kinetics of Divalent Metal Ions onto Pyrophyllite Using the Integral Method, Industrial and Engineering Chemistry Research, vol. 48(4) pp. 2125–2128, 2009
[5] Huang, W., Zhenshan, L., Niu, H., Li, D. and Zhang, J : Optimization of Operating Parameters for Supercritical Carbon Dioxide Extraction of Lycopene by Response Surface Methodology, Journal of Food Engineering, vol. 89, pp.298–302, 2008.
[6] Khataee, A. R., Gholamreza, D., Elahe, E. And Minoo, P : Central Composite Design Optimization of Biological Dye Removal in the Presence of Macroalgae *Chara* sp. Clean, Soil, Air, Water, vol. 38 (8), pp.750–757, 2010.
[7] Mabrouk, E., Ikram, J. and Mourad, B :Adsorption of Copper Ions on Two Clays From Tunisia: pH and Temperature Effects, Applied Clay Science, vol. 46, pp. 409–413, 2009
[8] Maiti, S.K. Handbook of Methods in Environmental Studies (1 and 2) ABD Publishers, Jaipur, 2004.
[9] Ninnekar, H.Z: Purification and properties of 2,3–dihydroxy–p–cumate–3,4–dioxygenase from Bacillus species, Biochemistry international, vol. 28, pp. 97–103, 1992.
[10] Noorjahan, C.M. and Jamuna, S: Physico–Chemical Characterisation of Brewery Effluent and Its Degradation using Native Fungus – *Aspergillus Niger*, *Aquatic Plant – Water Hyacinth– Eichhornia sp and* Green Mussel – *Pernaviridis,* Journal of Environment and Earth Science, vol. 2 (2), pp.31–40, 2012
[11] Sin, H. N., Yusof, S., Hamid, N. S. A. and Rahman, R. A: Optimization of enzymatic clarification of sapodilla juice using response surface methodology, Journal of Food Engineering, vol. 73, pp. 313–319, 2006.
[12] United Nations Environment Programme (UNEP). A snapshot of the world's water quality: towards a global assessment. Nairobi, 2016.
[13] Vazquez, M., Delgado, R. and Castro, A.J: Modelling of the enzymatic hydrolysis of potato (*Solanum tuberosum*) using response surface methodology, Starch, vol. 61, no. 10, pp. 601–609, 2009.
[14] Yi, S., Su, Y., Qi, B., Su, Z. and Wan, Y: Application of response surface methodology and central composite rotatable design in optimization; the preparation condition of vinyltriethoxysilane modified silicalite/ polydimethylsiloxane hybrid pervaporation membranes, Separation and Purification Technology, vol.71, pp.252–262, 2010.

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