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ADSORBENT TREATMENT OF COMPLEX INDUSTRIAL WASTEWATER: OPTIMIZATION OF PROCESS CONDITIONS BY RESPONSE SURFACE METHOD

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Abstract

The aim of this study was to use low cost adsorbent blend with synthetic zeolite in the treatment and Comparative study of the adsorbents respectively with the aim of detoxifying produced water before its safe disposal onto land or into water bodies. One week composite sampling was done every 2 hours, mixed properly and stored before the treatment processes commenced. Characterization was carried out on the produced water according to standard methods. The coconut shell and synthetic zeolite were afterward treated following standard procedures. Part of the treated coconut shell and zeolite were then mixed at ratio 1:1. The experimental parameters such as adsorbent dose and initial analytes concentrations, temperature and contact time were studied via design expert model. The optimum adsorption percentage occurred at adsorbent dose of 1 g, contact time at 120 minutes, pH value at 8, and temperature at 57 ^{0}C for all adsorbents were blend ratio zeolite/carbonized coconut shell was 97.33%, zeolite was 94.65% and carbonized coconut shell was 95.72%. The optimum adsorption percentage was achieved at 1 g/ 100 ml dose with blend ratio zeolite/carbonized coconut shell. High adsorption capacity and dimensionless separation parameters of the tested blend ratio zeolite/carbonized coconut shell fit and makes it preferable, cheap and environmentally friendly alternative adsorption material.

***Keywords*:** Adsorption, Industrial wastewater, Response surface method.

Introduction

Produced water is defined as the water that exists in subsurface formations and is brought to the surface during oil and gas production. Water is generated from conventional oil and gas production, as well as the production of unconventional sources such as coal bed methane, tight sands, and gas shale. The concentration of constituents and the volume of produced water differ dramatically depending on the type and location of the petroleum product. Produced water accounts for the largest waste stream volume associated with oil and gas production.

Produced water (PW) is the largest stream of wastewater generated by the petroleum industry during oil and gas field exploration and production and contains a wide range of hydrocarbons in free, dispersed and dissolved forms [1]. PW has a complex compound (organic and inorganic), such as grease, dissolved and dispersed oil, formation solids, scale products, heavy metals, waxes, radionuclides, dissolved oxygen, treating chemicals, dissolved gases, salts and microorganisms [2, 3, 4]. The aim of this study is to examine the adsorption of hydrocarbon in oil field produced water using blend of zeolite and activated carbon prepared from coconut shells.

Materials and Method

Sample preparation

The coconut shell was cleaned with deionized water and dried at 110 ^{0}C for 48 hours to reduce the moisture content. The dried samples were then crushed and sieved to a size range of 1-2mm. Subsequently, the coconut shell was carbonized in the furnace at 600 ^{0}C at the rate of 30 ^{0}C/min and held for 2 hours. After carbonization, it was allow to cool, then grind with a mechanical grinder to form powder. The powder was sieved to size fraction and then stored in teflon nylon bag.

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The zeolite was brought out from the reagent bottle and measured into a crucible and placed in an oven at 110 ^{0}C for 1 hour. After 1 hour it was brought out and placed in the dessicator and allowed to cool before being stored in a teflon bag. Part of the carbonized coconut shell was mixed with part of the zeolite in a stainless steel beaker with the weight ratio of zeolite/carbonized coconut shell equal to 1:1. The blend samples were placed in an oven at 110 ^{0}C for 1 hour. The product was cooled in a desiccator containing drying agent for 30 minutes and then placed in the furnace at 700 ^{0}C for 20 minutes. The furnace was turned off and the zeolite/carbonized coconut shell blend was removed from the furnace and placed in a dessicator and allowed to cool. It was then grind and packed in a teflon bag [5]. The produced adsorbents were then characterized and use for treatment of produced water [6].

Adsortption Experiment
The adsorption study basically involves adding a specified amount of the prepared adsorbents (carbonized coconut shell, zeolite and 1:1 ratio zeolite-carbonized coconut shell) with produced water. The setup were prepared in batches and were subject to varying conditions based on design expact model. The solutions were centrifuged at 120 rpm at varying time after which the solution was filtered and 10 ml of the solution were mixed with 10 ml of n-Hexane in a separating funnel. The n-Hexane was separated from the mixture after allowing complete separation in the separating funnel. The concentration of the total hydrocarbon was determined using the PG T180 UV-VIS Spectrophotometer. The varying condition at which the batch experiments was carried out includes the following, adsorbent dose, contact time, temperature, pH.

Result and Discussion
Table 1: Results of % Removal and Predicted value of Hydrocarbon content at varied parameters using ratio 1:1 blend of zeolite and carbonized coconut shell as adsorbent.

Std	Run	A:Adsorbent dosage (g)	B:Contact time (mins)	C:pH	D:Temperature (◦C)	Removal %	Predicted Value
13	1	0.55	5	6	57	79.14	79.08
29	2	0.55	62.5	8	57	90.91	90.80
25	3	0.55	62.5	8	57	91.44	90.80
20	4	1	62.5	10	57	91.44	91.69
6	5	0.55	62.5	10	32	82.89	82.87
7	6	0.55	62.5	6	82	88.24	89.01
23	7	0.55	5	8	82	81.82	80.56
28	8	0.55	62.5	8	57	90.37	90.80
21	9	0.55	5	8	32	73.88	72.21
9	10	0.1	62.5	8	32	83.23	84.71
5	11	0.55	62.5	6	32	85.03	85.70
3	12	0.1	120	8	57	94.12	93.09
24	13	0.55	120	8	82	94.12	94.48
17	14	0.1	62.5	6	57	90.37	88.81
14	15	0.55	120	6	57	91.98	92.47
4	16	1	120	8	57	97.33	96.94
1	17	0.1	5	8	57	74.33	75.47
18	18	1	62.5	6	57	88.77	88.46
10	19	1	62.5	8	32	86.63	86.22
8	20	0.55	62.5	10	82	89.3	89.38
2	21	1	5	8	57	78.07	79.85
26	22	0.55	62.5	8	57	90.37	90.80
19	23	0.1	62.5	10	57	84.1	83.10
12	24	1	62.5	8	82	94.65	93.73
27	25	0.55	62.5	8	57	90.91	90.80
22	26	0.55	120	8	32	93.05	93.00
11	27	0.1	62.5	8	82	86.03	87.01
16	28	0.55	120	10	57	94.58	95.20
15	29	0.55	5	10	57	73.82	73.89

Table 2: Model Summary Statistics

Source	Std.Dev.	R^2	AdjustedR^2	PredictedR^2	PRESS	
Linear	2.78	0.8476	0.8222	0.7868	259.42	
2FI	2.67	0.8944	0.8357	0.7657	285.08	
Quadratic	**1.21**	**0.9832**	**0.9664**	**0.9061**	**114.29**	**Suggested**
Cubic	0.9995	0.9951	0.9770	0.3846	748.62	Aliased

The **Predicted R^2** of 0.9061 is in reasonable agreement with the **Adjusted R^2** of 0.9664; i.e. the difference is less than 0.2

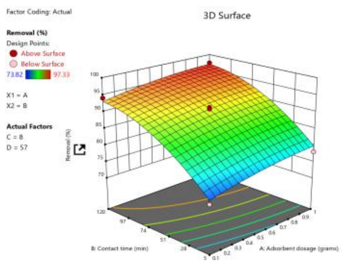


Figure 1: Contact time and adsorbent relationship 3D

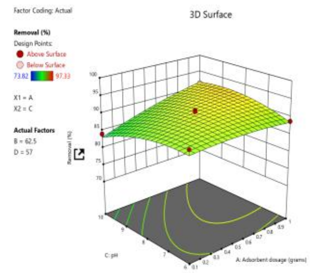


Figure 2: pH and adsorbent relationship 3D

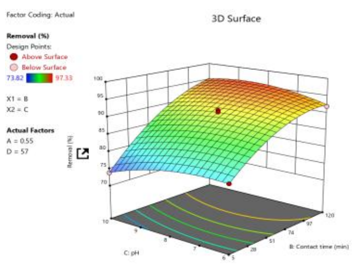


Figure 3: pH and contact time relationship 3D

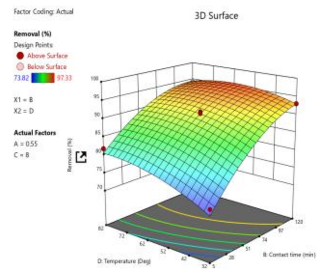


Figure 4: Temperature and contact time relationship 3D

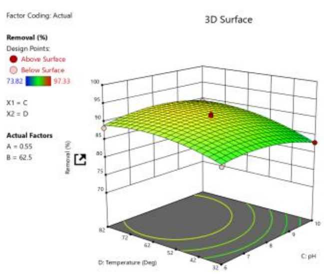


Figure 5: Temperature and pH relationship 3D

Table 3. Results of % Removal and Predicted value of Hydrocarbon content at varied parameters using Zeolite as adsorbent.

Std	Run	A:Adsorbent dosage (g)	B:Contact time (mins)	C:pH	D:Temperature ◦C	Removal %	Predicted %
13	1	0.55	5	6	57	73.8	73.84
29	2	0.55	62.5	8	57	87.7	87.59
25	3	0.55	62.5	8	57	87.7	87.59
20	4	1	62.5	10	57	87.7	87.61
6	5	0.55	62.5	10	32	78.07	77.98
7	6	0.55	62.5	6	82	83.96	84.58
23	7	0.55	5	8	82	78.07	76.46
28	8	0.55	62.5	8	57	87.7	87.59
21	9	0.55	5	8	32	67.55	66.29
9	10	0.1	62.5	8	32	78.94	80.38
5	11	0.55	62.5	6	32	80.75	81.55
3	12	0.1	120	8	57	90.37	89.36
24	13	0.55	120	8	82	91.44	91.05

17	14	0.1	62.5	6	57	84.49	82.94
14	15	0.55	120	6	57	88.24	88.60
4	16	1	120	8	57	94.65	94.65
1	17	0.1	5	8	57	70.05	70.58
18	18	1	62.5	6	57	87.17	86.90
10	19	1	62.5	8	32	83.42	82.57
8	20	0.55	62.5	10	82	87.17	86.90
2	21	1	5	8	57	74.33	75.88
26	22	0.55	62.5	8	57	87.7	87.59
19	23	0.1	62.5	10	57	82.35	80.98
12	24	1	62.5	8	82	91.98	91.65
27	25	0.55	62.5	8	57	87.17	87.59
22	26	0.55	120	8	32	89.3	89.26
11	27	0.1	62.5	8	82	81.28	83.25
16	28	0.55	120	10	57	90.91	91.99
15	29	0.55	5	10	57	68.45	69.20

Table 4: Response 1 Removal

Source	Sequential p-value	Lack of Fit p-value	Adjusted R^2	Predicted R^2	
Linear	< 0.0001	< 0.0001	0.8183	0.7836	
2FI	0.5086	< 0.0001	0.8142	0.7291	
Quadratic	**< 0.0001**	**0.0015**	**0.9698**	**0.9136**	**Suggested**
Cubic	0.4329	0.0007	0.9726	0.1749	**Aliased**

Table 5. Model Summary Statistics

Source	Std. Dev.	R^2	Adjusted R^2	Predicted R^2	PRESS	
Linear	3.10	0.8443	0.8183	0.7836	320.49	
2FI	3.13	0.8806	0.8142	0.7291	401.20	
Quadratic	**1.26**	**0.9849**	**0.9698**	**0.9136**	**127.97**	**Suggested**
Cubic	1.20	0.9941	0.9726	0.1749	1221.77	Aliased

Focus on the model maximizing the **Adjusted R^2** and the **Predicted R^2**.

Table 6. Response: Removal

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	1458.45	14	104.17	65.16	< 0.0001	Significant
A-Adsorbent dosage	84.11	1	84.11	52.61	< 0.0001	
B-Contact time	1057.69	1	1057.69	661.62	< 0.0001	
C-pH	1.18	1	1.18	0.7370	0.4051	
D-Temperature	107.22	1	107.22	67.07	< 0.0001	
AB	0.0000	1	0.0000	0.0000	1.0000	
AC	1.78	1	1.78	1.11	0.3089	
AD	9.67	1	9.67	6.05	0.0275	
BC	16.08	1	16.08	10.06	0.0068	
BD	17.56	1	17.56	10.98	0.0051	
CD	8.67	1	8.67	5.43	0.0353	
A^2	2.66	1	2.66	1.67	0.2177	
B^2	122.01	1	122.01	76.32	< 0.0001	
C^2	35.81	1	35.81	22.40	0.0003	
D^2	40.24	1	40.24	25.17	0.0002	
Residual	22.38	14	1.60			
Lack of Fit	22.16	10	2.22	39.44	0.0015	not significant
Pure Error	0.2247	4	0.0562			
Cor Total	1480.83	28				

The **Model F-value** of 65.16 implies the model is significant. There is only a 0.01% chance that an F-value this large could occur due to noise.

P-values less than 0.0500 indicate model terms are significant. In this case A, B, D, AD, BC, BD, CD, B^2, C^2, D^2 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.
The **Lack of Fit F-value** of 39.44 implies the Lack of Fit is significant. There is only a 0.15% chance that a Lack of Fit F-value this large could occur due to noise. Significant lack of fit is bad.
The model equation using blend of zeolite and carbonized coconut shell absorbent is

$$\boldsymbol{Y = 90.8 + 2.06A + 8.68B - 0.6167C + 2.45D - 0.1325AB + 2.24AC + 1.31AD + 1.98BC - 1.72BD + 0.8CD - 0.8046A^2 - 3.66B^2 - 1.98C^2 - 2.08D^2} \quad \textbf{(1)}$$

Table 7: Fit Statistics

Std. Dev.	**1.26**		R²	**0.9849**
Mean	83.53		**Adjusted R²**	0.9698
C.V. %	1.51		**Predicted R²**	0.9136
			Adeq Precision	31.1859

The **Predicted R²** of 0.9136 is in reasonable agreement with the **Adjusted R²** of 0.9698; i.e. the difference is less than 0.2

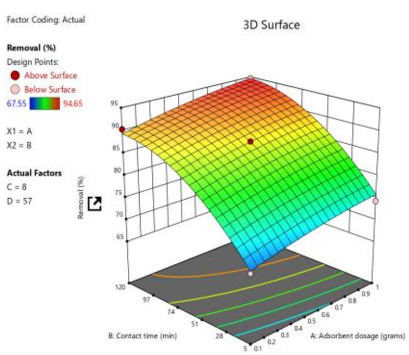
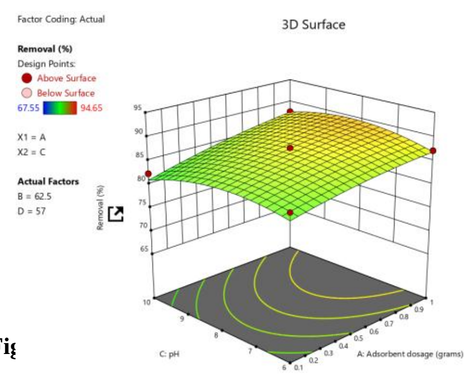


Figure 6: Contact time and adsorbent dosage relationship 3D



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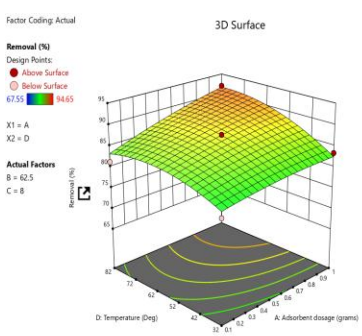

Figure 8: Temperature and adsorbent dosage relationship 3D

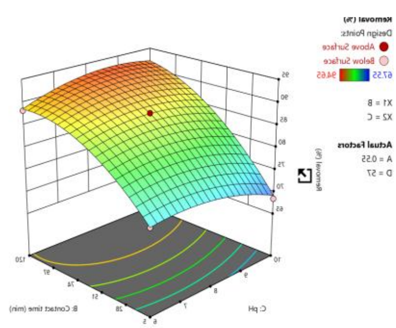

Figure 9: pH and Contact time relationship 3D

Table 8: Results of % Removal and Predicted value of Hydrocarbon content at varied parameters using Carbonized coconut shell as adsorbent.

Std	Run	A:Adsorbent dosage (g)	B:Contact time (mins)	C:pH	D:Temperature ◦C	Removal %	Predicted %
13	1	0.55	5	6	57	75.94	75.74
29	2	0.55	62.5	8	57	88.24	88.66
25	3	0.55	62.5	8	57	88.77	88.66
20	4	1	62.5	10	57	88.77	88.64
6	5	0.55	62.5	10	32	80.21	80.35

7	6	0.55	62.5	6	82	85.56	85.94
23	7	0.55	5	8	82	78.68	77.46
28	8	0.55	62.5	8	57	89.3	88.66
21	9	0.55	5	8	32	70.54	69.14
9	10	0.1	62.5	8	32	81.07	82.53
5	11	0.55	62.5	6	32	82.89	83.57
3	12	0.1	120	8	57	91.98	90.70
24	13	0.55	120	8	82	92.51	92.55
17	14	0.1	62.5	6	57	85.56	84.33
14	15	0.55	120	6	57	89.84	90.35
4	16	1	120	8	57	95.72	95.55
1	17	0.1	5	8	57	71.66	72.35
18	18	1	62.5	6	57	88.24	88.11
10	19	1	62.5	8	32	84.49	83.74
8	20	0.55	62.5	10	82	88.24	88.08
2	21	1	5	8	57	75.4	77.20
26	22	0.55	62.5	8	57	88.77	88.66
19	23	0.1	62.5	10	57	83.96	82.73
12	24	1	62.5	8	82	93.05	92.43
27	25	0.55	62.5	8	57	88.24	88.66
22	26	0.55	120	8	32	90.91	90.77
11	27	0.1	62.5	8	82	82.35	83.94
16	28	0.55	120	10	57	92.51	93.55
15	29	0.55	5	10	57	71.12	71.45

Table 9: Response Removal

Source	Sequential p-value	Lack of Fit p-value	Adjusted R^2	Predicted R^2	
Linear	< 0.0001	0.0009	0.8357	0.8044	
2FI	0.4749	0.0008	0.8343	0.7606	
Quadratic	**< 0.0001**	**0.0201**	**0.9697**	**0.9152**	**Suggested**
Cubic	0.2838	0.0150	0.9777	0.3961	**Aliased**

The **Predicted R^2** of 0.9152 is in reasonable agreement with the **Adjusted R^2** of 0.9697; i.e. the difference is less than 0.2.

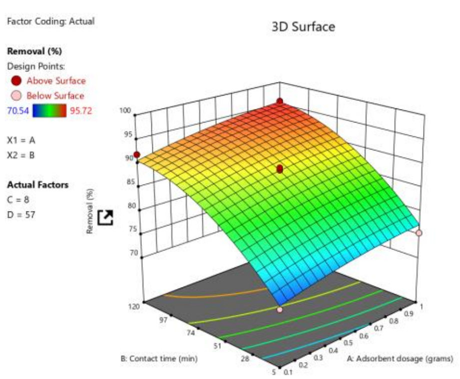

Figure 10: Contact time and adsorbent dosage relationship 3D

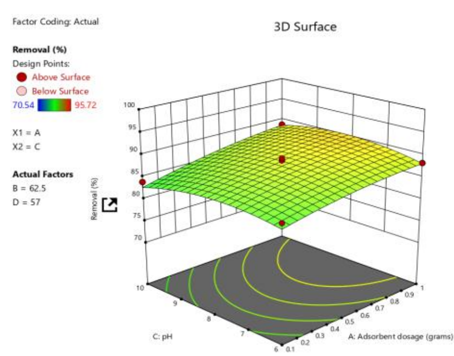

Figure 11: pH and adsorbent dosage relationship 3D

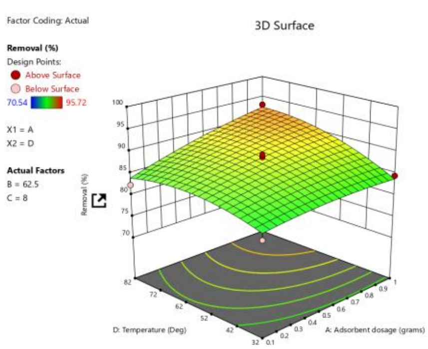

Figure 12: Temperature and adsorbent dosage relationship 3D

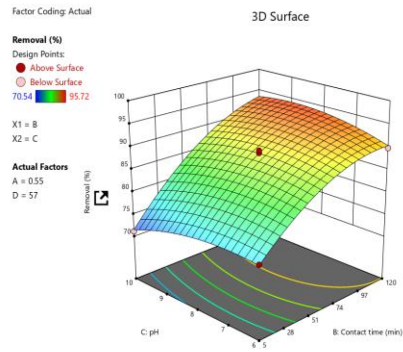

Figure 13: pH and Contact time relationship 3D

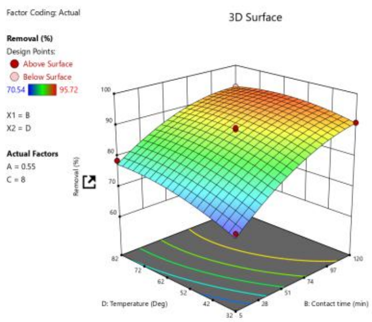

Figure 14: Temperature and contact time relationship 3D

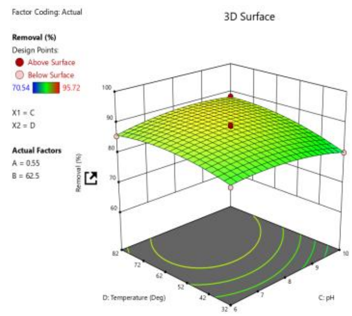

Figure 15: Temperature and pH relationship 3D

The results of the ratio blend zeolite/carbonized coconut shell showed that the highest adsorption capacity at 97.5 % removal which occurred at pH 8, Temperature 57 ^{0}C, Contact time of 120 minutes and dosage at 1 g compared to the other adsorbents. On the other hand, the lowest adsorption efficiency was recorded in the case of the zeolite at 94.5 % removal which occurred at pH 8, Temperature 57^{0}C, contact time of 120 minutes at dosage of 1 g . The R^2 value for the ratio blend zeolite/carbonized coconut shell shows the experimental to be 0.9832 that of the zeolite shows the experimental to be 0.9849, while that of the carbonized coconut shell shows the experimental to be 0.9849. The predicted R^2 value for all adsorbent is in reasonable agreement with the adjusted R^2 for each.

From the results obtained contact time is inevitably a fundamental parameters in all transfer phenomena such as adsorption. So, it is important to study its effect on the capacity of retention of hydrocarbon by the adsorbents (Srivastava VC, 2006). Results obtained from current study considering the required time for adsorption was in accordance with the results of Srivastava VC, 2006, Venckatesh et al, 2010, Husoon, 2011. From the results of present study it is possible to conclude the following subjects such as: removal efficiency of ratio 1:1 blend zeolite/carbonized coconut shell adsorbent have a significant ability in removal of hydrocarbon from produced water waste and affected by various environmental factors.

The pH of the adsorption process is an important controlling parameter in hydrocarbon adsorption process (Barrera et al, 2006). This parameter is directly related to the competition of hydrogen with carbon in covalent active sites on the adsorbent surface (Lodeiro et al, 2006). The optimum pH for hydrocarbon adsorption was laid between 6 and 8 in case of this study.

The temperature dependence of hydrocarbon adsorption by the adsorbents was studied over a range of 32-82 ^{0}C. The optimum percentage of adsorption of hydrocarbon at 120 minutes was found to be 97.5%, 95% and 94.5% respectively at 57 ^{0}C . In this model, the adsorbents is treated as being surrounded by a boundary layer film of water molecules through which the hydrocarbon must diffuse prior to adsorption on the adsorbents. The observation about the enhanced hydrocarbon adsorption rate by the adsorbent at higher temperatures are in perfect agreement with findings.

Conclusion

It can be concluded that all three adsorbents can be considered a low cost alternative for treatment of industrial effluents for toxic hydrocarbon removal before discharge into the environment.

The effective treatment of produced water for the removal / reduction in the parameters determined is among the most important issues for many industrialized countries.

Results obtained from the characterization of the materials showed that it has high potential to be employed as an effective adsorbent in removing hydrocarbon and would be useful for the design of treatment plants in most of our industries at a cheaper rate.

Acknowledgement
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