

Application of Response Surface Methodology for optimizing processing conditions for the adsorption of pollutants from refinery effluent of Oman

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Abstract

The present research work focused on the removal of pollutants from refinery waste water using date palm seed charcoal as adsorbent. A series of batch experimental studies were performed in the treatment of petroleum industry effluent by varying the adsorbent size (AS), contact time (CT) and adsorbent dosage (AD). The effectiveness of date palm seed activated carbon for the treatment of wastewater before and after is assessed by measuring the Chemical Oxygen Demand (COD), Biological Oxygen Demand (BOD), Total Organic Carbon (TOC), Total Dissolved Solids (TDS), Total Suspended Solids (TSS) and Turbidity. The statistical modeling of batch experiments for the optimization of processing parameters is carried out using Response surface methodology (RSM). The optimum processing conditions obtained are contact time =169.422 min, particle size =296.074 μm and adsorbent dosage =1gm. The optimum percentage removals of BOD, COD, TDS, TOC, TSS and Turbidity were found to be 84.048, 92.770, 91.667, 95.473, 95.650 and 88.423 respectively.

The equilibrium data corresponding to the optimum conditions were analysed using Langmuir and Freundlich adsorption isotherm models and the study shows that Freundlich model was found to be the best fit to describe the experimental data. Adsorption thermodynamic studies are also carried out and the results suggest that the system is endothermic, favorable and spontaneous in nature.

Keywords: Adsorbent, Contaminants, Isotherms, Response Surface Methodology, Statistical modeling.

Introduction

Rapid industrialization has created environmental issues which result in consistent release of toxic effluents. These toxic effluents are harmful to all living organisms, therefore clean freshwater is an essential ingredient for a healthy human life. Repossession and reuse of industrial effluent are a normal practice in the industries due to high utilization of process water in its production.^{1,2} Adsorption is a most famous approach employed for effluent removal with the utilization of different types of least expensive and easily

accessible materials from natural sources^{3,4}. These techniques have gained considerable attention due to their high pollution removal efficiency and offer better quality products. Moreover, the commercial usefulness of such process was well-established previously.^{5,6}

The batch adsorption tests were performed for the removal of chromium and nickel from wastewater using rice straw by varying the stirring time, adsorbent dosage and effluent solution pH.^{7,8} The optimum removal conditions of chromium and nickel were found to be very expeditious during the first 40 minutes for untreated rice straw and 50 minutes for treated rice straw, thereafter it remains stable. Adsorbent dosages were 8 g/100 ml and 12 g/100 ml of untreated rice straw for chromium and nickel respectively and for treated rice straw it was found to be 8 g/100 ml for both the metals. Numerous investigators⁹⁻¹⁵ studied the treatment of wastewater using similar types of low-cost adsorbents derived from similar agricultural waste materials.

Another study¹⁶ studied the elimination of organic matter from domestic effluents by using coconut coir activated carbon as adsorbent. The result shows the reduction of the pollution parameters viz. color, COD and BOD by 75 to 80 percent removal of contaminants. The study concluded that the isotherms can be used to enhance charcoal columns. Another study used similar adsorbent and opined that those adsorbents are economical, eco-friendly and sustainable.¹⁸ The brief information of fluoride removal by batch adsorption technique using date palm seeds is presented. Activated carbon was used as adsorbent for the study. The analysis exhibits that the exhilarating chemical behaviour of carbon (IR=0.75) raises surface area of the activated carbon and the efficiency of fluoride removal¹⁹.

Date seeds were used broadly in effluent treatment due to its huge adsorption capacity and fiber content consisting of hydrophilic groups/radicals. Hydroxyl radicals are strong oxidants that will react and oxidize the organic substance in wastewater. Agro waste products are expressed as an acceptable source for preparation of activated carbon because of their perpetual availability and viable activity for extracting broad spectra.¹⁹ The adsorption quality of charcoal from date seeds is commonly led by the surface area of charcoal due to pore formation and surface functional groups.

The major crop in the Sultanate of Oman is date palm (*Phoenix dactylifera* L.), possessing nearly 49 percentage of

sophisticated area which is 82 percent of entire fruit crops produced in the country. During the year 2005, production of dates was about 238,000 metric tonnes. Thereby, date palm generates huge quantity of seed waste since the date pits weigh 0.5 g to 4 g and represent 6 to 20% of the fruit weight depending on maturity, variety and grade.^{23,28} These seeds may be utilised for production of activated carbon to be used as pollutant adsorbents for industrial water treatment.²¹

Prepared activated carbon from the date seeds of Phoenix dactylifera (a true date palm) has been reported to act as the good adsorbent compared to 13 different species of phoenix and has the adsorption capacity of 61.7 mg/g used for the treatment of petroleum industries waste water. The contaminants present in the effluents can split into organic and inorganic matters which includes heavy metals, nitrogen, phosphorous, ammonia and iron chlorides. The organic matter and ammonia nitrogen are studied as principal chemical attributes present in the effluent.²⁰ Other parameters such as COD and BOD are used to characterize organic matter in effluent. Additionally, TDS, TSS, TOC, turbidity and amount of heavy metals such as zinc and chromium were determined in petroleum wastewater of Oman.

The current study focused on the preparation of activated carbon from Oman date palm seeds and coated with polymer called surface modified activated carbon. The surface modified carbon has more tendency to adsorb the contaminants present in petroleum wastewaters. The processing parameters varied in the study are stirring time, adsorbent size and dosage on the reduction of different pollution parameters of industrial effluents. Initially, the adsorption tests were carried out through batch experimentation and the initial sample data was used for parameter optimisation using RSM software. Later experimental data were fitted with suitable isotherms suggested by Freundlich and Langmuir. The thermodynamic analysis was also conducted.²¹⁻²³

Material and Methods

Phosphoric acid, sodium hydroxide and HCl of analytical grade are procured from Sigma Aldrich. High purity Millipore water of conductivity 18Ω was used throughout the experiment. The adsorption studies were performed at room temperature in a rotary shaker at a stirring speed of 100 rpm. The final concentration was analyzed after adsorption process using BOD analyzer Eutech Instrument WP PCD 650, TOC analyzer Shimadzu TOC-LCSH/CSN. The TDS, TSS and turbidity were analyzed by Eutech T100 and COD removal analyzed by Orion Instrument COD AQ 400

Preparation of adsorbent from date palm seeds: Date seeds were collected from local market of Sultanate of Oman. The possessed date seeds were washed thoroughly with distilled water followed by drying under sun. After drying, 1.785 kg of date seeds was soaked in 500 ml of

phosphoric acid for 24 hours and transferred into a metallic cylinder and kept in a furnace at 450°C for 3 hours to yield the activated carbon granules. The resulting granules were crushed into different sizes ranging from 150 μm to 1mm followed by washing with distilled water till the pH reaches 7.0. After washing, activated carbon granules were dried in drying oven at 105°C for an hour and then ground into fine granules and sieved into desired particle size and also coated with polymer called surface modified activated carbon.

Characterization of Adsorbent: The physical characterization of the adsorbent of 296.074μm size was analyzed using BET analyzer. The surface morphologies of adsorbent derived from date seeds were analyzed using SEM at an excitation voltage of 20.0 kV and at a magnification 1000 X.

Batch Adsorption Studies: Batch experimental studies were performed using the prepared adsorbent for the removal of pollutants from refinery waste water by varying the contact time, adsorbent size and adsorbent dosage. The experiments were performed by mixing 200 ml of refinery waste water samples with specified amount of adsorbent and stirred at a speed of 100 rpm for a specified time. After adsorption process, the treated wastewater samples were filtered and analyzed for COD, TDS, TSS, DO, BOD, TOC and Turbidity.

Design of Experiments (DOE): The factors influencing the parameters such as adsorbent dosage (AD), contact time (CT) and adsorbent size (AS) for the effective removal of contaminants were studied with a standard RSM design called Composite Central Design (CCD). RSM software technique assists to enumerate the output variables which are known as responses (Y) and input variables termed as factors (X):

$$Y = f(X_1, X_2, X_3, \dots, X_n) \quad (1)$$

CCD supports to optimize the parameters with minimal number of experiments. It analyses the interaction between the parameters.²³ In the current study, the processes are having three independent variables, therefore “n” is equal to three, thus the total number of experiments required is given in equation (2):

$$N = 2^n + 2n + n_c = 2^3 + 2X_3 + 6 = 20 \quad (2)$$

The center points are used to assess the experimental errors. In this study, the BOD, COD, TDS, TOC, TSS and turbidity are responses (Y) of the system while the process parameters, (AD) 1.0-5.0 g, (CT) 60-180 min and (AS) 165-880μm are input parameters.

$$Y = \beta_0 + \sum_{i=1}^n \beta_i X_i^2 + \sum_{i=1}^n \beta_i X_i + \sum_{i=1}^n \sum_{j=1}^{n-1} \beta_{ij} X_i X_j \quad (3)$$

ANOVA was also used to determine a linear relationship between an independent variable and a dependent variable.

The range of CT, AD and AS was 60 to 180 min, 1.0 to 5.0gms and 165 to 880µm respectively as shown in table 1. Statistical experimental design is presented in table 4.

Table 1
Input factors and range of experimental design of parameters for removal of contaminants

Factors	-1	0	1
CT (mins)	60	120	180
AD (gm)	1	3	5
AS (µm)	165	522.5	880

Thermodynamic Studies: In this study, the adsorption of both Zinc and Chromium at four different temperatures (303 K, 313 K, 323 K and 333 K) was estimated. The increase in temperature favours the transport of adsorbate within the pores of sorbent and raise in sorption sites achieved as a result of breaking of few internal bonds adjacent to the rim of active sites. Thermodynamic parameters have been determined to study the nature of adsorption process.

ICP- AES Analysis: Ultra-Trace Element Detection and Component Analysis from highly precise analytical equipment has the large scope of its application and is currently being used for accurate and quantitative determination of element concentrations, determination of major and minor trace elements in water. This equipment incorporates DUAL View (i.e. Both Axial and Radial) to accommodate the analysis of high sensitivity as well as high concentration water samples (such as Seawater, Brackish Water, Industrial effluent etc.)

Results and Discussion

Figure 1 and figure 2 display the micro structural characterization of activated carbon before and after treatment. The BET surface area and its properties are shown in table 2.

Table 2
Physical Properties of adsorbent

Physical properties	Values
BET Surface area (m ² kg ⁻¹)	463791
Pore volume (m ³ kg ⁻¹)	0.000011784
Micro pore area (m ² kg ⁻¹)	23354.6
Bulk density (kg/m ³)	1025

As seen from figure 1, the particles are scattered in nature whereas the Scanning electron micrograph of activated carbon after treatment shows a thick and clustered structure indicating the successful treatment of refinery waste water. The dark spots represent the deposition of pollutants on the surface of activated carbon.

The physio chemical characteristics of raw wastewater sample before treatment are shown in table 3.

Statistical Analysis and Model Fitting: The process parameters of CT, AD and AS were optimized by RSM considering BOD, COD, TDS, TSS, TOC and turbidity as the responses.

RSM was used to optimize the studied parameters (i.e. CT, AD and AS) for removal of BOD, COD, TDS, TSS, TOC and turbidity. The output (responses) are presented in table 5.

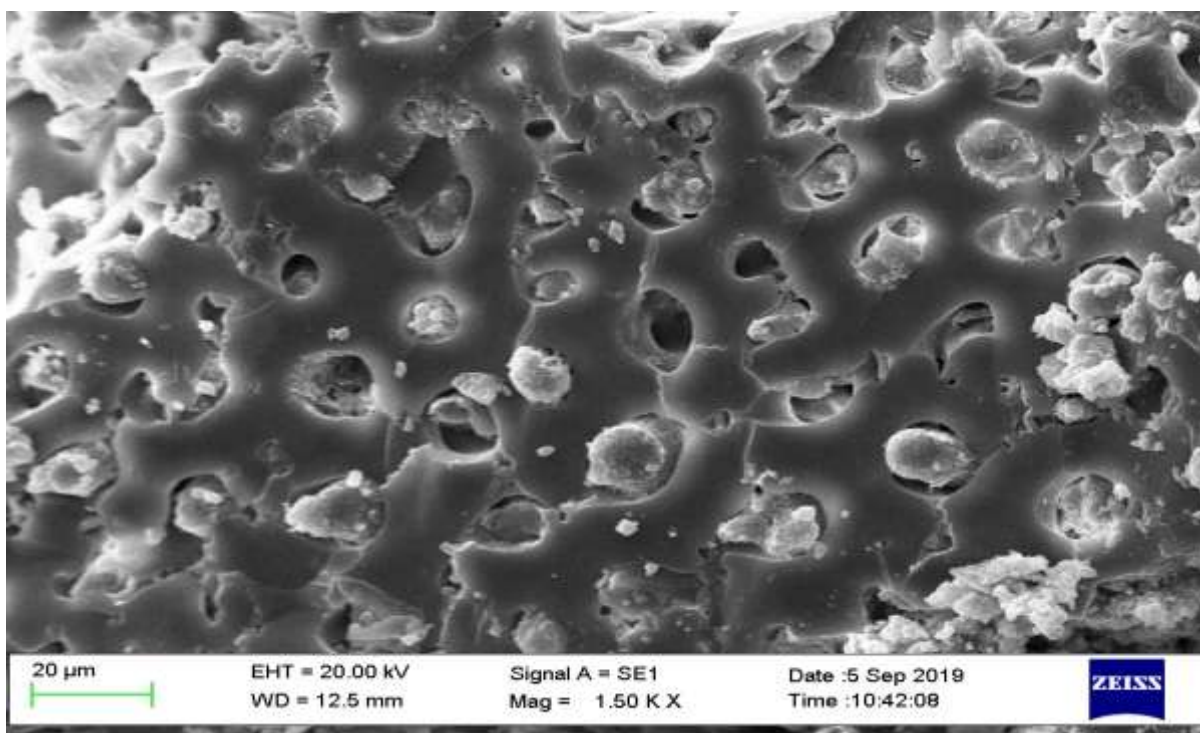


Figure 1: SEM image of adsorbent before treatment corresponding to a magnification of 1000 X

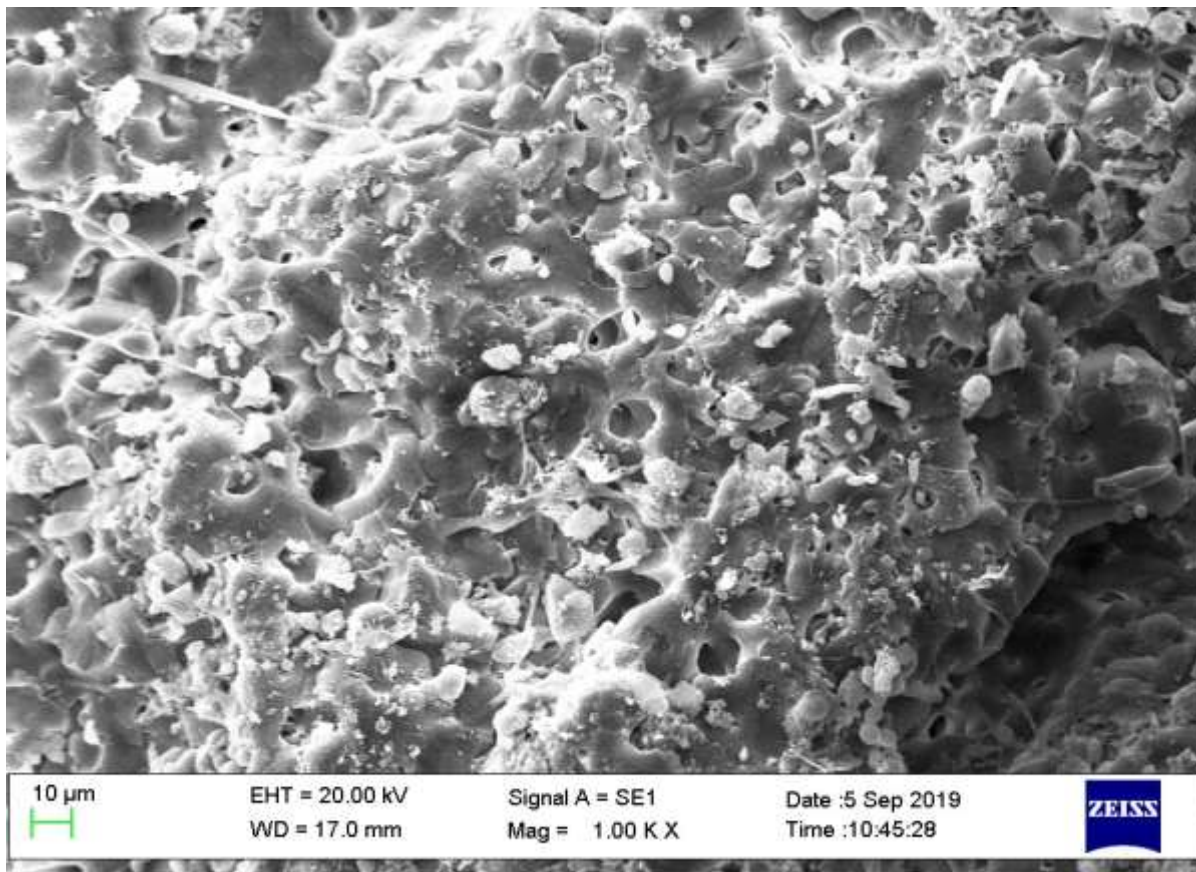


Figure 2: SEM image of adsorbent after treatment

Table 3
Characteristics of Wastewater sample before treatment

Parameters	value
COD	1240
BOD ₅	856
pH	8.46
TSS	310
TDS	3600
Color	3175
Turbidity	411
Ammonia nitrogen	42
Nitrate	3.385
Alkalinity	136
Phosphorus	1.70
Sulphide	16
Sulphate	45
TOC	390
Oil and grease	73
Phenol	1.30
Toluene	39.83
Ethylbenzene	1.85
Benzene	33.85
Xylene	31.54

(Turbidity units in NTU, other units are in ppm and for colour)

Table 4
Parameters analyzed after effluent treatment for statistical experimental design

Standard Run	Factor1 A:Contact time, mins	Factor2 B:adsorbent dosage, gms	Factor3 C:adsorbent size, micro-meter	Response 1 % BOD removal ppm	Response 2% COD removal ppm	Response 3 %TDS removal ppm	Response 4%TSS removal ppm	Response 5%TOC removal ppm	Response 6 % Turbidity removal NTU
1	60	3	522.5	80.18	79.22	73.05	77.87	81.80	84.9
2	120	3	522.5	80.52	84.39	85.97	82.83	83.38	83.56
3	60	5	880	78.61	75.97	76.38	61.53	61.53	76.3
4	120	5	880	78.35	69.06	79.16	70.24	78.02	73.54
5	120	5	165	82.09	85.71	82.08	78.62	85.46	81.1
6	180	3	522.5	80.51	85.45	86.11	81.31	85.76	83.76
7	60	3	522.5	80.52	81.13	75.33	81.78	81.78	85.76
8	60	1	165	84.91	88.18	88.55	86.87	86.43	86.94
9	120	5	522.5	79.79	90.25	91.08	87.78	87.78	83.54
10	60	1	880	77.63	81.16	74.44	88.23	88.23	84.9
11	180	3	165	83.54	82.85	91.13	74.10	74.10	82.88
12	120	3	522.5	81.06	85.55	86.11	85.08	85.58	85.53
13	180	3	522.5	80.50	86.75	89.22	85.46	86.19	85.7
14	60	3	522.5	81.02	81.03	91.38	78.50	78.50	84.88
15	180	3	165	83.66	78.15	91.66	72.91	72.91	81.1
16	120	3	522.5	80.51	85.55	87.5	82.43	91.08	83.58
17	120	1	165	83.67	80.61	86.16	88.23	88.23	87.79
18	120	3	522.5	79.78	84.41	86.25	82.20	86.31	88.66
19	120	1	880	79.70	81.68	91.63	93.82	95.47	73.78
20	180	5	165	81.06	81.16	91.25	82.97	82.28	76.7

Table 5
Values obtained from isotherm models at optimum conditions of contact time 169.422 mins and 296.074 μm size

Model	Parameters								
	BOD removal			COD removal			TOC Removal		
	Sm	K _L	R ²	Sm	K _L	R ²	Sm	K _L	R ²
Langmuir Isotherm Model	0.226	7.817	0.970	6.116	17.96	0.982	0.115	54.09	0.979
Freundlich Isotherm Model	N	K _F	R ²	N	K _F	R ²	N	K _F	R ²
	2.161	0.294	0.958	9.267	5.865	0.974	1.719	0.505	0.997

Final equations are shown in equations (4), (5), (6), (7), (8) and (9) in terms of coded factors. At least twenty number of experiments were required to know the coefficients of quadratic model equation and six responses of the system.

$$R_1 = +80.74 + 0.4857A - 0.7493B - 2.32C - 0.3162AB - 0.0581 + 0.632BC \quad (4)$$

where R₁ = BOD, A = CT, B = AD, C = AS

$$R_2 = +84.81 + 0.6842A - 2.44B - 3.50C - 1.31AC - 1.99BC - 4.06A^2 + 7.65B^2 - 7.92C^2 \quad (5)$$

where R₂ = COD

$$R_3 = +87.30 + 1.74A - 1.58B - 3.21C - 3.25AB + 1.1BC - 11.01A^2 + 6.08B^2 + 1.25C \quad (6)$$

where R₃ = TDS,

$$R_4 = +84.630 + 1.04A - 7.94B - 2.89C + 0.0148AB + 2.50AC - 4.60BC - 1.91A^2 + 12.79B^2 - 12.16C^2 \quad (7)$$

where R₄ = TSS,

$$R_5 = +84.94 + 3.28A - 6.53B - 2.25C + 1.78AB + 2.79AC - 4.65BC + 0.712A^2 + 10.5B^2 - 13.10C^2 \quad (8)$$

where R₅ = TOC,

$$R_6 = +85.05 - 1.27A - 3.24AB - 2.98C + 1.70AB - 2.18AC + 1.01BC - 0.8994A^2 + 1.91B^2 - 5.95C^2 \quad (9)$$

where R₆ = Turbidity.

The 3D surface graph which is not shown in figure indicates the BOD at maximum removal of 84.048% which includes

good interaction between dosage and contact time. Similar trends were observed for the combined effect of CT, AS and also for AD, AS for percentage removal of BOD. High similarity between predicted and actual was obtained.

COD with respect to effect of time, AD and AS is shown in figure 3(a), figure 3(b) and figure 3(c). The 3D surface graph in figure 3(c) indicates the COD removal at 92.77% which

shows maximum removal of contaminants present in wastewater. Similar trends shown for figure 3(a) and figure 3(b). Actual vs. predicted plot figure 3(d) also shows a tremendous similarity between the predicted and the experimental values. The model has achieved the hypothesis of the ANOVA which is not shown and also reproduced the accuracy and suitability of RSM to enhance the process factors for the COD removal.

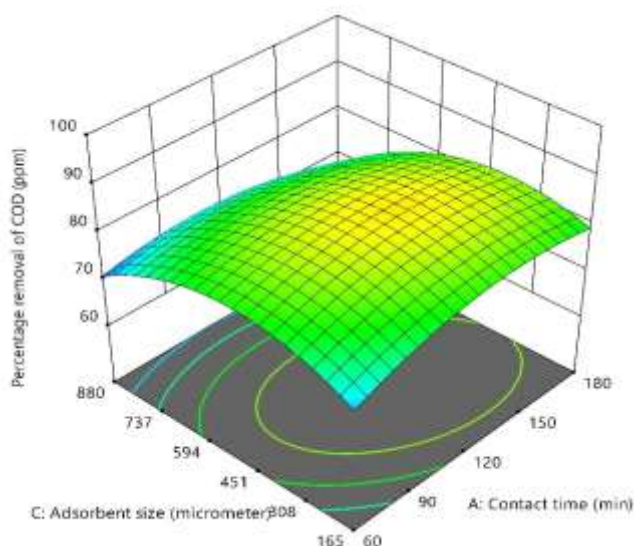


Figure 3a: 3D Surface plot with counter diagram presenting the influence of dosage and time on COD removal.

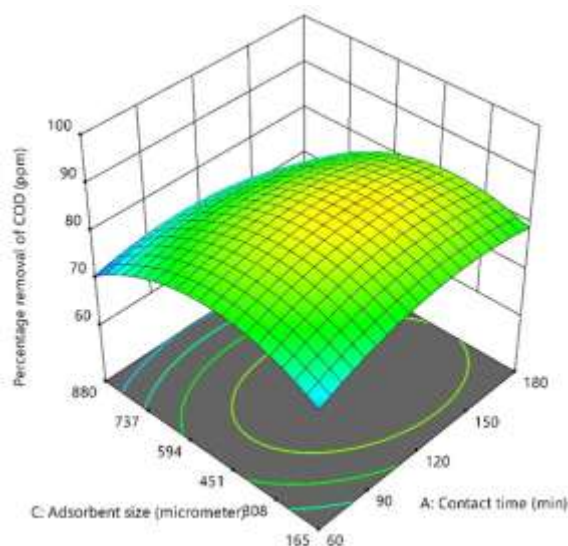


Figure 3b: 3D Surface plot with counter diagram presenting the influence of size and time on COD removal.

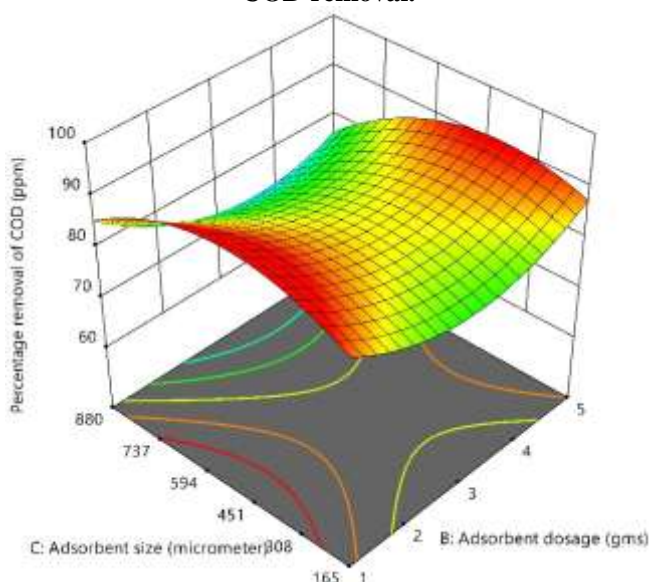


Figure 3c: 3D Surface plot with counter diagram presenting the effect of adsorbent size and adsorbent dosage on COD removal

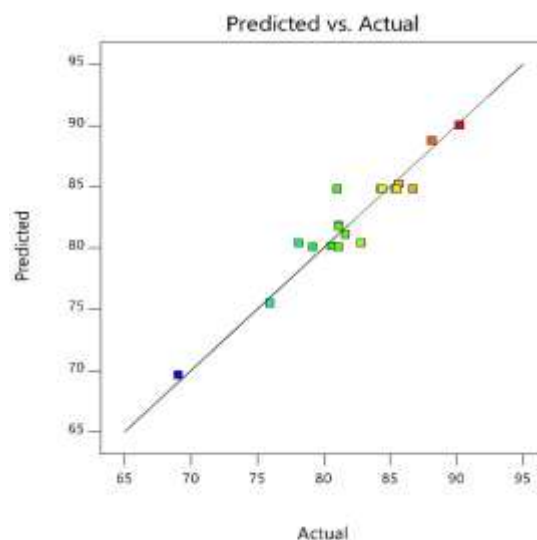


Figure 3d: 3D Surface plot with counter diagram presenting the COD removal Predicted vs actual

The 3D surface graph in figure 4(a) indicates the maximum removal of TDS at 91.66%, similar trends are shown for figure 4(b) and figure 4(c). Predicted vs. actual plot in figure 4(d) also represents a highest similarity which is noted between the experimental and predicted values. It is

henceforth achieved that the model has gratified the assumptions of the ANOVA.

Responses found for turbidity not shown in figure also show good result with effect of AS and AD with maximum

removal of turbidity at 88.423%; similarly the response found for TOC removal is observed at 95.47% for effect of dosage and time and also response found for maximum

removal of TSS is observed at 95.65% for combined effect of size and dosage, trends have been noticed for two combined effects of CT, AD and AS.

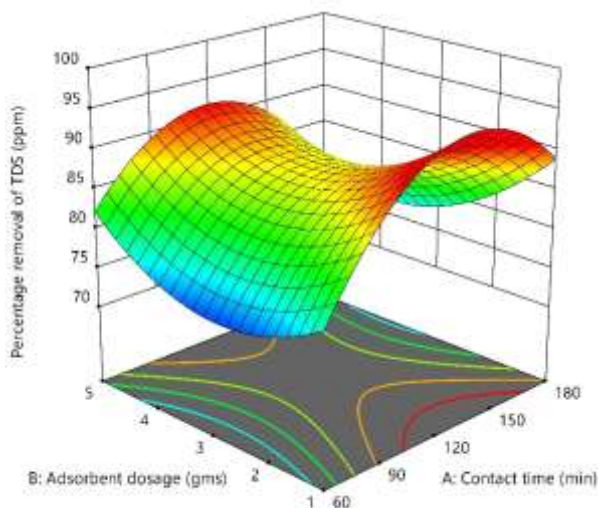


Figure 4a: 3D Surface plot with counter diagram showing the effect of dosage and time on TDS removal

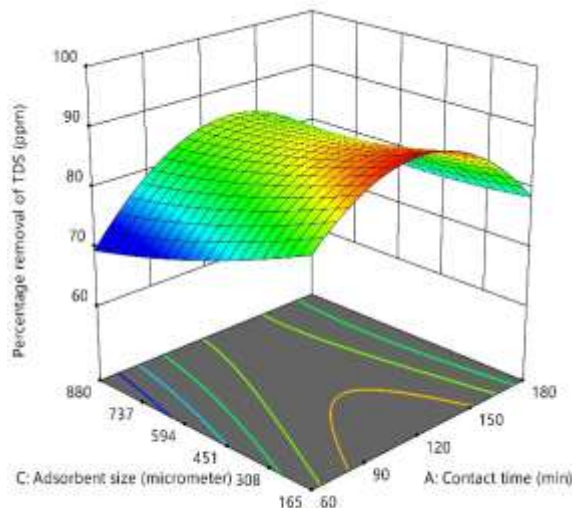


Figure 4b: 3D Surface plot with counter diagram showing the effect of size and time on TDS removal

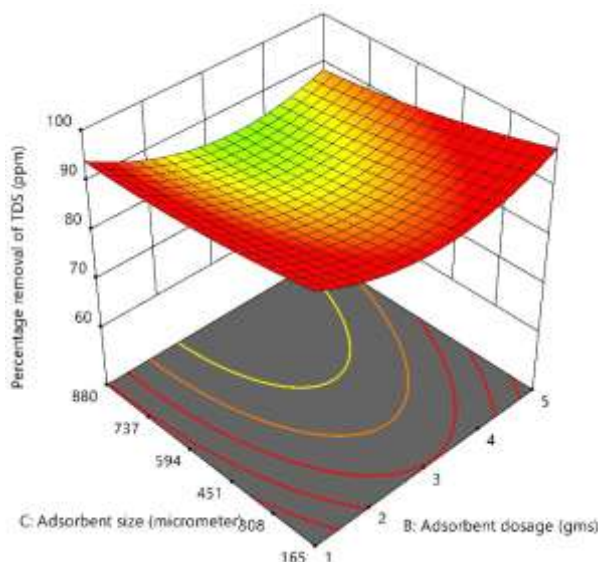


Figure 4c: 3D Surface plot with counter diagram showing the effect of size and dosage on TDS removal

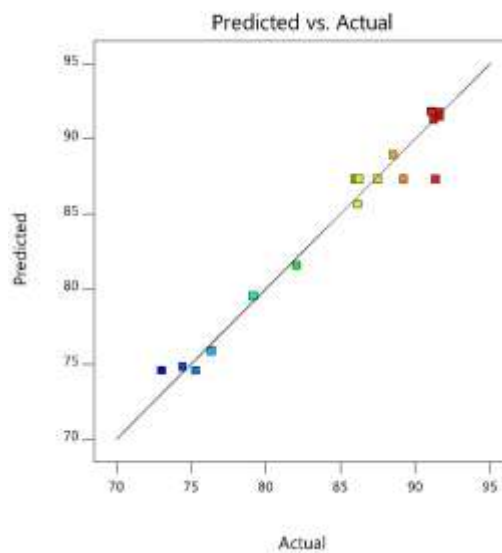


Figure 4d: 3D Surface plot with counter diagram showing the effect of size and dosage on TDS removal

A higher value of correlation coefficient confirms a good correlation among the independent variables. The integrity of fit for equation (4) to (9) was correlated with R (coefficient of expansion) and R^2 (co-efficient of determination) and analysed between the predicted and experimental values. The experimental results show $R^2 = 0.9595$ for the percentage removal of BOD, $R^2 = 0.9159$ for the percentage removal of COD, $R^2 = 0.9584$ for the percentage removal of TDS, $R^2 = 0.9549$ for the percentage removal of TSS, $R^2 =$

0.9112 for the percentage removal of TOC and $R^2 = 0.9377$ for the percentage removal of turbidity. Therefore regression model explains well.

Fitting of Optimum Data with Isotherm Models: The isotherm models Freundlich model and Langmuir model are given by equations (10) and (11) respectively. Experiments have been made to fit the following two linear isotherm models with the batch experimental data.

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \tag{10}$$

$$\frac{C_e}{q_e} = \frac{C_e}{S_m} + \frac{1}{K_L S_m} \tag{11}$$

In this present study, Langmuir and Freundlich isotherm models are used to study the adsorption. Previous literature shows that the Langmuir adsorption isotherm is predominantly used for adsorption that exists at peculiar sites of a homogenous adsorbent. Once the adsorbate molecules occupy completely the sites of adsorbent, equilibrium exists and further adsorption will not take place. Eq. (11), the Langmuir linear equation, characterizes the saturation of the monolayer curve.^{24,25}

The type of isotherm can be categorized into irreversible (R = 0), favorable (0 < R < 1) or unfavorable (R > 1). A graph of C_e/q_e versus C_e is plotted for Langmuir adsorption isotherm. The regression coefficient is noticed to be 0.979 for TOC removal.

The Freundlich adsorption isotherm model could have been expected if the binding energy changes continuously from site to site on solid surfaces^{26,27}. In adsorption process, multilayer adsorption mechanism takes place on a heterogeneous surface. The Freundlich adsorption isotherm is expressed by eq. (10).

The slope is n and the intercept is K_F presented in table 5, these values were found to be 1.719 and 0.505 respectively. R² of 0.997 was obtained for Freundlich adsorption isotherm for the parameter TOC removal. The obtained data shows that the Freundlich adsorption isotherm best fits than the Langmuir adsorption isotherm.

Thermodynamic Studies: The Gibbs's energy change ΔG⁰ was determined using eq. 12²⁴.

$$\Delta G^0 = -RT \ln K_a \tag{12}$$

$$K_a = \frac{C_a}{C_e} \tag{13}$$

Gibbs free energy change and the equilibrium constant can be represented using as:

$$\Delta G = \Delta H - T\Delta S \tag{14}$$

H⁰ and ΔS⁰ were obtained from figure 11 and 12. In K_a vs. 1/T is shown in table 6.

The adsorption process for zinc and chromium metal ions was favorable and spontaneous in nature as manifested by ΔG⁰ and ΔH⁰ values. In the present study ΔH is positive; therefore, adsorption is endothermic in nature. The rise in temperature results in rise in K_a²⁴. The significance of the ΔH⁰ value for physical adsorptions is between 2.1 to 20.9 kJ/mol while for chemical adsorption it is in the range of 80 to 200 kJ/mol. ΔH⁰ value for removal of Zinc is observed at 5.175 kJ/mol onto the activated carbon from date seeds from petroleum wastewater as low compared to chromium removal which is at 9.73 kJ/mol. The values of ΔS⁰ were reported for both zinc and chromium adsorption onto activated carbon.

Conclusion

Elimination of contaminants from refinery wastewater using date palm carbon was studied by varying the stirring time, adsorbent size and adsorbent dosage. Activated carbon from date seeds was prepared using phosphoric acid as activating agent. Characterization of the adsorbent was carried out using SEM and BET analysis. Massive reduction of organic pollutants was observed in terms of percentage removal of turbidity, COD, BOD, TSS, TOC and TDS. The experimental outcomes have been optimized by RSM.

The optimum contact time was observed to be 169.422 minutes, 296.074 μm adsorbent size and 1g adsorbent dosage. The optimum responses for maximum removal of BOD value have been found to be 84.048 %, COD 92.77 %, TDS 91.667 %, TSS 95.65 %, TOC 95.473 % and turbidity 88.423%.

Table 6
Thermodynamic data for adsorption of Zinc and Chromium metals onto activated carbon from date seeds

System	Temperature (K)	ΔG ⁰ (kJ/mol)	ΔH ⁰ (kJ/mol)	ΔS ⁰ (J/mol K)	R ²
Zinc	303	-5.34	5.1758	34.82	0.967
	313	-5.78			
	323	-6.05			
	333	-6.42			
Chromium	303	-13.24	9.7307	75.94	0.989
	313	-14.10			
	323	-14.84			
	333	-15.53			

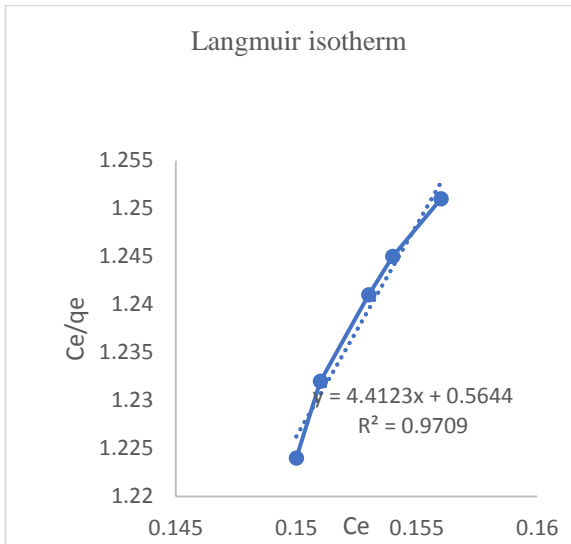


Figure 5: Langmuir Isotherms for BOD removal

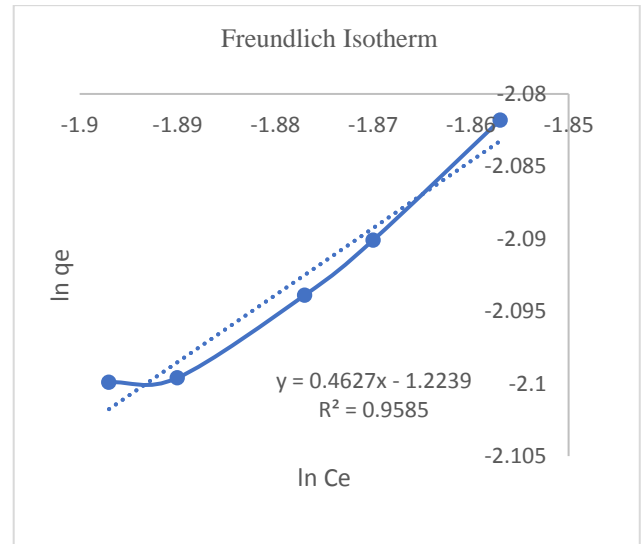


Figure 6: Freundlich Isotherms for BOD removal

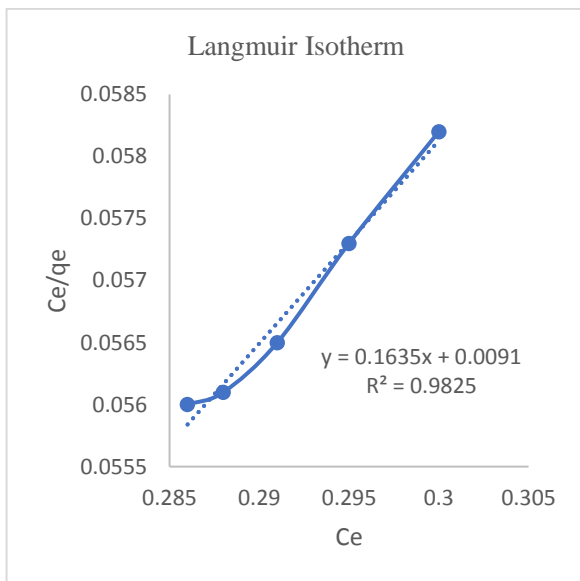


Figure 7: Langmuir Isotherms for COD removal

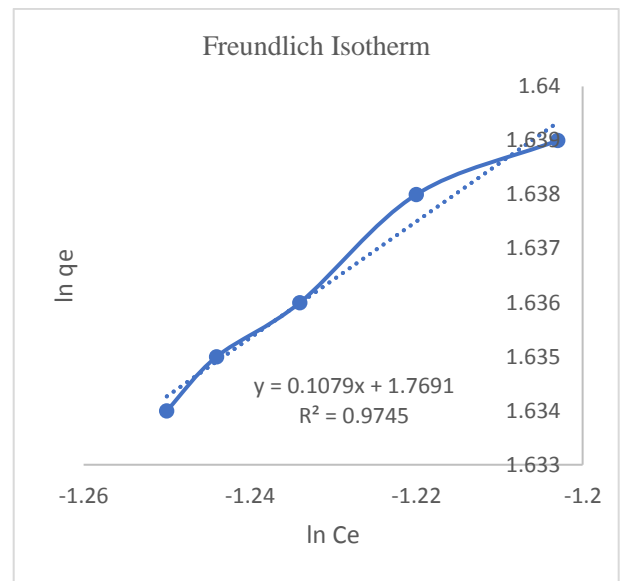


Figure 8: Freundlich Isotherms for COD removal

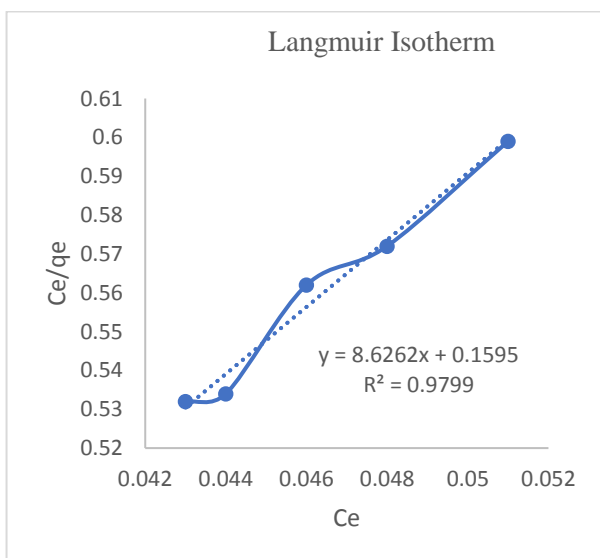


Figure 9: Langmuir Isotherms for TOC removal

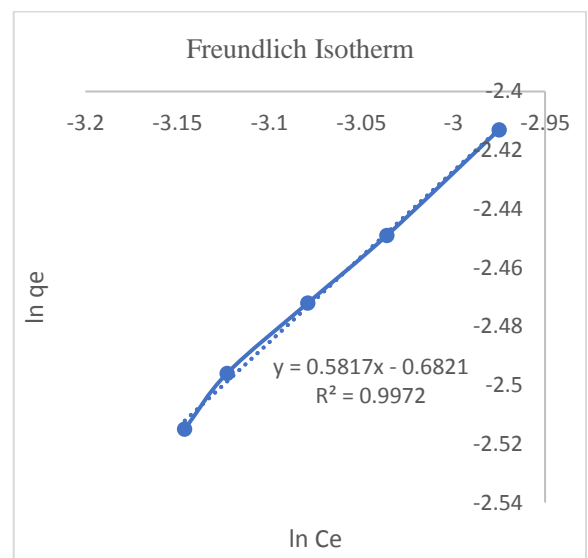


Figure 10: Freundlich Isotherms for TOC removal

Table 7
General survey for the treatment of petroleum effluents disclosed by various investigators

S.N.	Procedure	The wastewater type	Removed pollutants	Max. Removal efficiency (%)
1	The system of two stage BAF and UASB reactor.	Heavy oil wastewater	NH3-N	90.2
			COD	90.8
			Oil	86.5
2	The system of Anaerobic packed-bed biofilm reactor and UASB	Petroleum wastewater	COD	81.07
3	The sequencing batch reactor system	Petroleum wastewater	Phenols	98
4	Anaerobic submerged fixed-bed reactor (ASFBR)	Petroleum wastewater	COD	91
			TSS	92
5	Batch studies using date seeds activated carbon	Petroleum wastewater	BOD	84.04
			COD	92.77
			TDS	91.66
			TOC	95.47
			TSS	95.65
			Turbidity	88.423

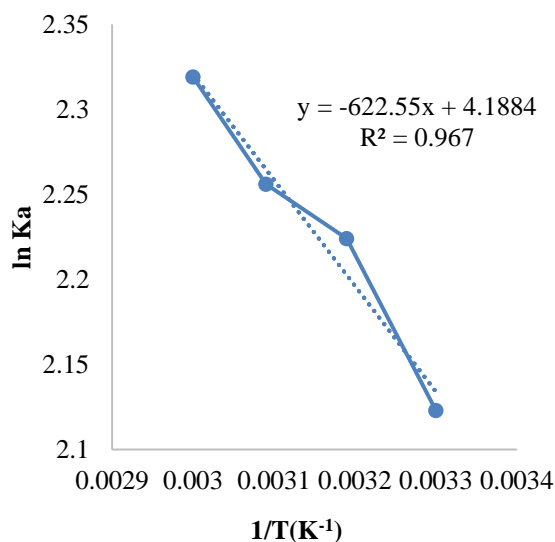


Figure 11: Thermodynamic plot of zinc adsorption on to date seeds activated carbon

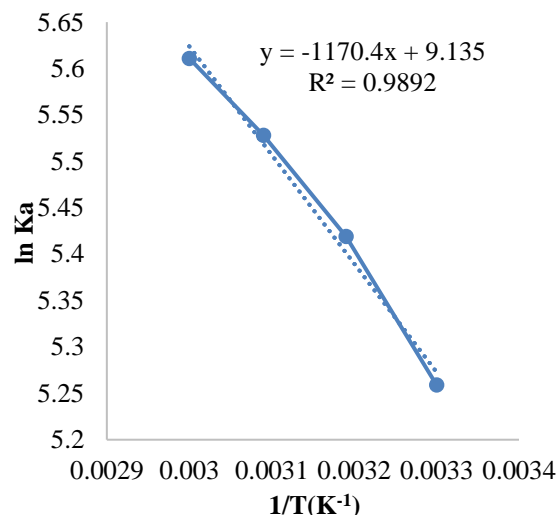


Figure 12: Thermodynamic plot of chromium adsorption on to date seeds activated carbon

Among the Freundlich and Langmuir isotherm models, the experimental results fit well with the Freundlich model in the current case with a better R^2 value of 0.997 for TOC removal. The thermodynamic studies revealed that the process is favorable, endothermic and spontaneous. Thereby, it was achieved that the prepared adsorbent could be effectively used for the treatment of effluent possessed from the petroleum refinery of Oman.

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References

1. Abu-Safa S., Abu-Salah M. and Gharaibeh S., Low-cost pre-treatment of pharmaceutical Wastewater, *Int. J. of Chemical, Molecular, Nuclear, Materials and Metallurgical Eng*, **6(2)**, 143-147 (2012)
2. Aljuboury D., Al A., Palaniandy P., Bin Abdul Aziz H. and Feroz S., Evaluating the TiO₂ as a solar photocatalyst process by response surface methodology to treat the petroleum wastewater, *Karbala Int. J. Modern Sci.*, **1**, 78-85 (2015)
3. Al Khusaibi T., Dumaran J., Geetha Devi M., Rao Nageswara L. and Feroz S., Treatment of dairy wastewater using orange and banana peels, *J. Chem. and Pharm. Res.*, **7(4)**, 1385-1390 (2015)

4. Alshabanat M., Rasmiah S., Al-Mufarij and Al-Senani M.G., Study on adsorption of malachite green by date palm fiber, *Orient J. Chem.*, **32(6)**, 3139-3144 (2016)
5. Ardestani F. and Abbasi M., Poultry Slaughterhouse Wastewater Treatment Using Anaerobic Fluid Bed Reactor and Aerobic Mobile-Bed Biological Reactor, *Int. J. Eng. – Transactions B: Applications*, **32(5)**, 634-640 (2019)
6. Al-Yahyai R. and Sulaiman Al-Khanjari, Biodiversity of date palm in the Sultanate of Oman, *African J. Agri. Res.*, **3(6)**, 389-395 (2008)
7. Brahmaiah T., Spurthi L., Chandrika K., Kausalya Chandra L., Yashas S., Ramanaiah S. and Sai Prasad K.S., Removal of heavy metals from wastewater using low cost adsorbent, *Int. J. Trend in Res. and Dev.*, **3(1)**, 63-69 (2016)
8. Brahmaiah T., Spurthi L., Chandrika K.S., Ramanaiah S. and Sai Prasad K.S., Kinetics of heavy metal (Cr & Ni) removal from the wastewater by using low cost adsorbent, *World J. Pharm. and Pharm. Sci.*, **4(11)**, 1600-1610 (2015)
9. Chatterjee S., Kumar A., Basu S. and Dutta S., Application of Response Surface Methodology For methylene blue dye removal from aqueous solution from low cost adsorbent, *Chemical Engineering Journal*, **181-182**, 289-299 (2012)
10. Chittala G. and Mogadati P., Performance studies on a pharmaceutical Wastewater treatment plant with a special reference to total dissolved solids removal, *International J. Life Sci. Biotech. and Pharma Res.*, **1**, 103-112 (2012)
11. Feroz S., Geetha Devi M. and Hamimy Said and Al S., A Comparative study on adsorption of chromium (VI) using high molecular weight crab shell chitosan and date seed carbon, *J. Chitin and Chitosan Sci.*, **1**, 111-115 (2013)
12. Feroz S., Nageswara Rao L., Kamalakar D. and Rao Venkateshwara M., Equilibrium, kinetic and thermodynamics studies of methylene blue dye from aqueous solution by using natural adsorbent, *Int. J. of Pharm. Chem. and Biolo. Sci.*, **4**, 960-967 (2014)
13. Feroz, S., Prasad V.S.R.K. and King P., A study on treatment of metallic effluents using activated charcoal, *J. Inst. of Eng.*, **86**, 12-15 (2005)
14. Hameed B.H., Salman J.M. and Ahmed A.L., Adsorption isotherm and kinetic modelling of 2, 4-D pesticide on activated carbon derived from date stones, *J. Haz. Mat.*, **163**, 121-126 (2009)
15. Hanum F., Bani O. and Izdiharo A.M., Characterisation of (Na₂CO₃) treated rice husk activated carbon and adsorption of lead from car battery wastewater? *Material Science and Engineering*, **180**, 1-12 (2017)
16. Hussein F., Athab Z., Ahmed F.H., Abbas J.L. and Zahra H.A., Preparation and characterization of activated carbon from Iraqi khestawy date palm, *J. Chem*, **1**, 1-8 (2015)
17. Karunya S., Feroz S., Al Harassi S. and Kishore S., Treatment of Oman pharmaceutical industry wastewater using low cost adsorbents, *J. Multidis. Eng. Science and Tech.*, **2(3)**, 339-341 (2015)
18. Keerthi B.G., Adsorption on fluoride removal by using batch techniques, *Indian J. Sci. Res.*, **12(1)**, 209-213 (2015)
19. Kulkarni S.J., Removal of organic matter from domestic wastewater by Adsorption, *International Journal of Science Engineering and Technology Research*, **2(10)**, 1836-1839 (2013)
20. Lova S.K., Tan M.C., Chinb N.L. and Tana K.W., Comparative Studies on Ultrasound Pre-treated Peanut Husk Powder and Ultrasound Simultaneous Process on Heavy Metal Adsorption, *Int. J. Eng. – Transactions B: Applications*, **31(8)**, 1334-1340 (2018)
21. Mukhopadhyay D., Sarkar J.P. and Dutta S., Optimization of process parameters for the economical generation of biogas from raw vegetable wastes under the positive influence of plastic materials using response surface methodology, *J. Biochem. Techn.*, **4(1)**, 549-553 (2013)
22. Mwangi G.M. and Oguntimein G.B., Study of an activated carbon system for the treatment of fermentation wastewater from a bioethanol production process, *The West Indian J. Eng.*, **35(2)**, 65-71 (2013)
23. Shahrina S., Lau W.J., Goha P.S., Jaafara J. and Ismaila A.F., Adsorptive Removal of Cr(VI) and Cu(II) Ions from Water Solution using Graphene Oxide–Manganese Ferrite (GMF) Nanomaterials, *Int. J. Eng. – Transactions B: Appl.*, **31(8)**, 1341-1346 (2018)
24. Smith J.M. and Van Ness H.C., Introduction to chemical engineering thermodynamic, Singapore, McGraw-Hill, <https://www.feedipedia.org/node/687> (1987)
25. Tanweer Ahmad, Mohammed Danish, Mohammed Rafatullah, Amira Ghazali, Othman Sulaiman, Rokiah Hashim, Mohammed Nasir and Mohammed Ibrahim, The use of date palm as a potential adsorbent for wastewater treatment: a review, *Env. and Sci. Poll. Res.*, **5**, 1464 -1484 (2012)
26. Vasantharaj S., Sathiyavimal S. and Hemashenpagam N., Treatment of municipal wastewater with special reference to activated carbon combined with sand, *Archives of Applied Sci. Res.*, **5(3)**, 90-92 (2013)
27. Younis A.S., Waleed A., Nour Sh G., Qarani A.S., Yasser M.M., Abdul A.H. and Abu A.S., Application of Response Surface Methodology to Enhance Phenol Removal from Refinery wastewater by Microwave process, *Int. J. Microwave Sci. and Tech.*, **2014**, 1-13 (2014)
28. Thirumalairaj J., Sivasankari K., Natarajaseenivasan K. and Balagurunathan R., Potential anti-leptospirosis compound, leptomycin B from marine Streptomyces indiaensis MSU5: taxonomy, fermentation, compound isolation, *in vitro* and *in vivo* efficacy, *World J. Microbiol. Biotechnol.*, **33**, 187 (2017).

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